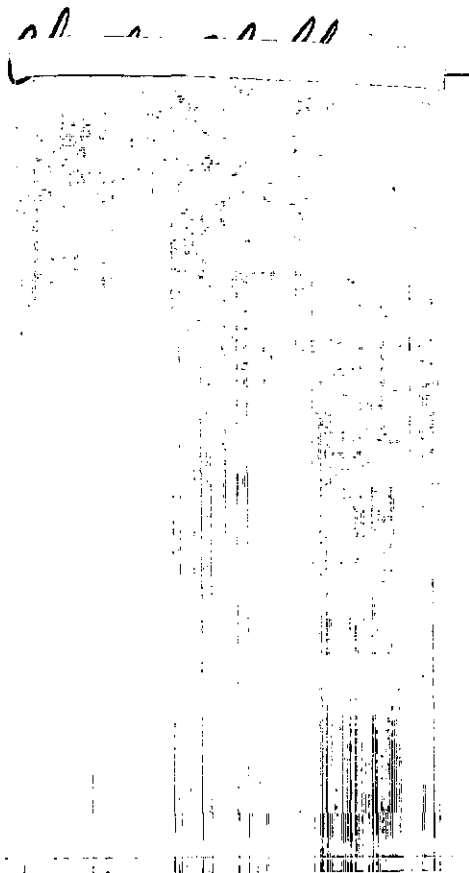


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REACTIONS OF ALLYL CHLORIDE, ALLYLTRI-  
METHYLAMMONIUM CHLORIDE, AND CYCLOPROPYLTRIMETHYL-  
AMMONIUM IODIDE WITH SODIUM IN LIQUID AMMONIA

A THESIS

Presented to

the Faculty of the Graduate Division

by

Charles Edward Collum

In Partial Fulfillment

of the Requirements of the Degree

Master of Science in Chemistry

Georgia Institute of Technology

September, 1964

REACTIONS OF ALLYL CHLORIDE, ALLYLTRI-  
METHYLAMMONIUM CHLORIDE, AND CYCLOPROPYLTRIMETHYL-  
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Date approved by Chairman: Nov. 4, 1964

# DEDICATION

Dedicated to Debbie Lee Holloway for the time she so graciously gave and the sacrifices she made during the preparation of this thesis and for what the future holds as she and I prepare to begin our lives together.

## ACKNOWLEDGEMENTS

The author would like to thank Dr. Wm. M. Spicer for teaching assistantships. He is deeply grateful to Dr. Erling Grovenstein, Jr. for suggesting this work, for the many suggestions for doing the work, for the many helpful discussions concerning the work, and for the patience to see that the work was done. He is also grateful for the research grant from the Atomic Energy Commission which was made available by Dr. Grovenstein.

The author would like to express his appreciation for the encouragement given him by his mother and brothers during his graduate work at Georgia Tech.

Because of the use of this thesis as a report, special permission was received from the Graduate Division to follow a format which varies in some respects from standard requirements.

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## SUMMARY

This work was carried out with three things in mind: (1) to study the cleavage of quaternary ammonium salts by sodium in liquid ammonia and determine qualitatively and quantitatively the products of cleavage; (2) to see if allyltrimethylammonium chloride can be isomerized by a strong base such as potassium amide in liquid ammonia; and (3) to determine by the use of radioactive allyl-1-C<sup>14</sup> chloride the mechanism for the reaction of allyl chloride with sodium in liquid ammonia to form diallyl.

The cleavage of 3-chloropropyltrimethylammonium chloride resulted in the formation of propane, propylene, cyclopropane, and methane with the yield of each hydrocarbon varying from run to run and the total yield of hydrocarbons varying from 12 to 82 per cent. This cleavage is believed to be complicated because of the heterogeneous nature of part of the reaction.

Cyclopropyltrimethylammonium iodide was cleaved with sodium in liquid ammonia to give mostly cyclopropane and methane. It was found that the ratio of cyclopropane to methane varied with the quantities of reactants used and with the mode of addition of reactants. This variation is thought to result from cleavage of the cyclopropyl group as a free radical and cleavage of methyl as a carbanion; with increasing concentration of sodium, cleavage of methyl as a carbanion becomes more favored.

The allyltrimethylammonium chloride was cleaved a total of eight times with the sodium to salt ratio varying from 2.2 to 60. The order of addition of reactants was also varied. It was found that the ratio of higher molecular weight hydrocarbons to methane remained constant over all reactions with a value of  $2030 \pm 320$ . This constancy is a good indication that both allyl and methyl are cleaved as carbanions since the ratio does not change over the wide range of concentrations studied.

The isomerization of allyl-1- $C^{14}$ -trimethylammonium chloride was carried out using potassium amide in liquid ammonia. The amide was formed by adding potassium to liquid ammonia and letting the mixture stand in the absence of a catalyst. The isomerized compound was cleaved with sodium after destroying the potassium amide with ammonium chloride. Radiochemical assay of the propylene produced indicated that some isomerization occurred under the conditions investigated.

When allyl chloride is reacted with sodium in liquid ammonia bialllyl and isomers of bialllyl are produced along with propylene. The main purpose of this research was to try to determine the mechanism of the reaction of allyl chloride with sodium to form bialllyl by the use of carbon-14 as a tracer. Three different mechanisms are considered along with molar activities expected for each mechanism.

Two runs were made using allyl-1- $C^{14}$  chloride. The analyses of the first run were not all reliable so a second run was made. The results of the first run gave a good indication that the mechanism consists of an  $S_N2$  displacement of allyl carbanion upon allyl chloride. The second run indicated that there could be a simultaneous  $S_N2'$  dis-

placement of allyl carbanion upon allyl chloride or alternately some formation of bialllyl by coupling of allyl free radicals. The results, however, could also be explained by ionization of allyl chloride in liquid ammonia or by the bialllyl undergoing a Cope rearrangement in the v.p.c. during separation. The final conclusion is that most or possibly all of the bialllyl is formed by  $S_N2$  displacement of allyl carbanion upon allyl chloride.

## CHAPTER I

### INTRODUCTION

Reductive Cleavage of Allyl Compounds with Metals.--The reduction of compounds by dissolving metals seems to occur not with "nascent" (or atomic) hydrogen but with electrons and protons supplied from different sources. It has been shown that alkali metals dissolve in liquid ammonia with dissociation into electrons and metal ions.<sup>1,2</sup> The question as to when protons enter the reducible system can not generally be answered. In some cases, the protons need not be involved at all in order for reduction to occur.

For reductive cleavage of quaternary ammonium halide Emde<sup>4</sup> has suggested that the ammonium salt dissociates into alkyl halide and tertiary amine. The alkyl halide is then reduced by sodium and water to hydrocarbon. Grovenstein and co-workers<sup>5</sup> have presented an

---

1. (a) C. A. Kraus, J. Am. Chem. Soc., **30**, 653 (1908); (b) S. Freed and N. Sugarman, J. Chem. Phys., **11**, 354 (1943).

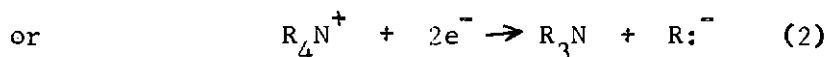
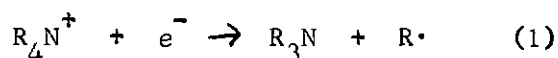
2. M. C. R. Symons, Quart. Rev. (London) **13**, 99 (1959).

3. R. L. Letsinger and J. G. Traynham, J. Am. Chem. Soc., **70**, 3342 (1948).

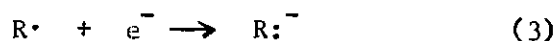
4. (a) H. Emde, Arch. Pharm., **247**, 314 (1909); (b) H. Emde and H. Kull, ibid., **272**, 469 (1934).

5. E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon, and R. W. Stevenson, J. Am. Chem. Soc., **81**, 4842 (1959).

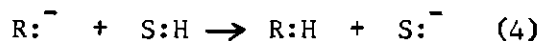
argument against this mechanism for the reductive cleavage reaction. They have presented two possible mechanisms, the carbanion mechanism and the free radical mechanism.<sup>6</sup> The electron transfer to a quaternary ammonium cation may consist of one-electron or two-electron addition in the cleavage step:



The radical produced in equation 1 may be reduced to a carbanion:



The final product then results from proton transfer from the solvent S:H



These mechanisms leave some questions unanswered, thus whether the cleavage occurs during or after the electron addition and, for the two-electron addition, whether the two electrons add stepwise or simultaneously.

This general scheme of reductive cleavage has been discussed by Birch.<sup>7</sup> The influence of structure upon reaction rate was such to suggest that cleavage occurred by two-electron addition. Hazlehurst,

---

6. E. Grovenstein, Jr., and R. W. Stevenson, *ibid.*, **81**, 4850 (1959).

7. A. J. Birch, *Quart. Rev. (London)* **4**, 69 (1950).

8. D. A. Hazlehurst, A. K. Holliday, and G. Pass, *J. Chem. Soc.*, 4655 (1956).

Holliday, and Pass<sup>8</sup> have suggested that the cleavage of tetra-n-alkylammonium halides was by one-electron addition. Their chief evidence was the formation of traces of ethane from methylammonium halides.

The principal evidence that proton transfer occurs after rather than simultaneously with the formation of carbanions is that cleavage<sup>6</sup> of tetraalkylammonium halides with sodium gave similar ratios or products in liquid ammonia and dioxane even though dioxane is a poorer donor than liquid ammonia.

It was concluded by Grovenstein and co-workers<sup>6</sup> that methyl and the higher primary alkyl groups probably cleave from nitrogen as carbanions while secondary and tertiary alkyl groups predominately cleave as free radicals. While the relative rates of cleavage are primarily due to stabilizing or destabilizing effect of  $\alpha$ -alkyl groups upon incipient carbanions or radicals in the transition state for cleavage, secondary and especially tertiary alkyl groups may be assisted by steric acceleration. Reductive cleavage also involves the formation of amines as well as hydrocarbons so differences in stability of amines could affect the relative rates of reductive cleavage. The more basic the amine the less readily it might be expected to be formed by reductive cleavage.

Krug and Tocker<sup>9a</sup> studied the reductive cleavage of n-alkyl sulfides, allyl sulfides, allyl mercaptans, and thiophene in liquid ammonia in presence of ammonium ions. The metals most often used in

---

9. (a) R. C. Krug and S. Tocker, J. Org. Chem., 20, 1 (1950).

cleavage were sodium and lithium. It was observed that a metal with a high cell potential favors a greater reduction of the organic compound than a metal of lower potential. The authors suggested the formation of carbanions as possible intermediates during their cleavage studies.

Wepster and his co-workers<sup>9b</sup> have considered the possibility of both an ionic mechanism (via carbanions) and a free radical mechanism for the reaction of alkyl halides with sodium in liquid ammonia. They found that the reduction of optically active 6-chloro-2,6-dimethyloctane to 2,6-dimethyloctane by a solution of lithium, sodium or potassium in liquid ammonia proceeds predominantly with retention of configuration and they concluded that the reaction most probably proceeds via carbanions.

In the present work an attempt is made to study cleavage of quaternary ammonium salts by determining the hydrocarbon products from the reaction along with the ratio of the products.. Also the plan is to study the reaction of allyl-1-C<sup>14</sup> chloride with sodium to determine the mechanism of the reaction. If the allyl chloride reacts as a free radical the formaldehyde formed by ozonization of biallyl would contain one-half of the original molar radioactivity of the allyl chloride. On the other hand, if the biallyl is formed by an S<sub>N</sub>2 reaction of allyl carbanion upon allyl chloride the formaldehyde would contain one-fourth

---

9. (b) A. Beverloo, M. C. Dieleman, K. S. deVries, P. E. Verkade, and B. M. Wepster, Koninkl. Nederl. Akademie van Wetenschappen, Proceedings, Series B, No. 5, 445 (1956). A. Beverloo, M. C. Dieleman, P. E. Verkade, K. S. deVries, and B. M. Wepster, Rec. Trav. Chim. Pays-Bas, 81, 1033 (1962); P. E. Varkade, K. S. deVries, and B. M. Wepster, ibid., 82, 637 (1963); P. E. Verkade, K. S. deVries, and B. M. Wepster, ibid., 83, 367 (1964).



of the original molar radioactivity of the allyl chloride.

Reactions of Some Allyl-1-C<sup>14</sup> Compounds.--Recently some reactions of allyl-1-C<sup>14</sup> compounds have been reported by Nystrom and co-workers.<sup>10</sup> The normal bimolecular nucleophilic displacement, S<sub>N</sub>2, has been observed in the following reactions: conversion of allyl-1-C<sup>14</sup> chloride to allyl-1-C<sup>14</sup> ethyl ether, transformation of allyl-1-C<sup>14</sup> chloride to diethyl allyl-1-C<sup>14</sup>-malonate,<sup>11</sup> and the reduction of allyl-1-C<sup>14</sup> chloride to propene-3-C<sup>14</sup> by lithium aluminum hydride. The unimolecular substitution, S<sub>N</sub>1, has been observed in the following reactions: solvolysis of allyl-1-C<sup>14</sup> chloride in 99.5 per cent formic acid, and the formation and subsequent hydrolysis of allyl-1-C<sup>14</sup> and allyl-3-C<sup>14</sup> magnesium chloride to propene-C<sup>14</sup>. Results not explainable on the basis of one of the more common mechanisms are: the solvolysis of allyl-1-C<sup>14</sup> chloride to allyl-1-C<sup>14</sup> alcohol by silver hydroxide and water, and the deamination of allylamine-1-C<sup>14</sup> by nitrous acid in water and acetic acid.

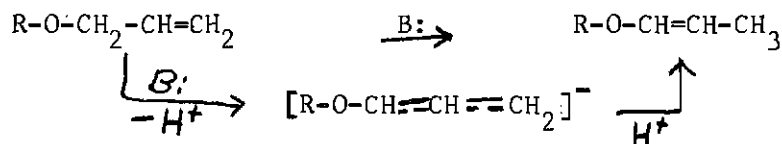
Rearrangement of Some Allylic Compounds by Bases.--The base catalyzed rearrangement of an allyl ether to a propenyl ether apparently represents a further example of that group of reactions classified

---

10. C. R. A. Berger, J. C. Leak, C. C. Neto, and R. F. Nystrom, p. 48-0, Abstracts of 137th Meeting of American Chemical Society, in Cleveland, Ohio, April, 1960.

11. C. R. A. Berger, Dissertation Abstracts, 21, 2105 (1961).

as true, three-carbon prototropic shifts.<sup>a</sup> Prosser<sup>12</sup> found that a



number of allyl ethers are rearranged to propenyl ethers at 150-175° in the presence of the basic catalyst, potassium t-butoxide. Certain color changes are observed during the reaction. A yellow mixture was obtained upon addition of a catalyst to the substrate. When the mixture was heated, the yellow color changed to orange to orange-red. The final product was usually light yellow. The color of the reaction mixture indicated the reaction to be a carbanion reaction as proposed in the above equation. In most cases, the yield was 90-95 per cent cis-isomers for each reaction.

Price and Snyder<sup>13</sup> found that in the isomerization of allyl sulfides by base the solvent had a very large effect on the rate of isomerization and that allyl sulfides are isomerized by a carbanion mechanism to propenyl sulfides. The cis-isomer in these reactions is not produced in nearly as large quantity as in the allyl ether rearrangement. They

---

a. A true, three-carbon prototropic system is defined as one in which the nature of the activating group is such that covalency changes beyond the limits of the three-carbon system itself are structurally excluded, i.e., the negative charge on the allylic anion is located within the limits of the system itself. (J. W. Baker, "Tautomerism" D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 80).

12. T. J. Prosser, J. Am. Chem. Soc., **83**, 1701 (1961).

13. C. C. Price and W. H. Snyder, J. Am. Chem. Soc., **83**, 1773 (1961); (b) C. C. Price and W. H. Snyder, J. Org. Chem., **27**, 5639 (1962); (c) C.C. Price and W. H. Snyder, Tetrahedron Letters, No. 2, 69 (1961).

also found that when allyl amines are treated with potassium t-butoxide in dimethyl sulfoxide mostly cis-propenyl amines are obtained. Vinyl allyl ether is converted to vinyl propenyl ether by treatment with metallic sodium or alkoxide ion.<sup>14</sup>

Ingold and Rothstein<sup>15</sup> studied the interconversion of  $\text{Na}, \text{Na}, \text{Na}$ -methyldiethyl- $\text{N}\gamma, \text{N}\gamma, \text{N}\gamma$ -triethyl- $\Delta\alpha$ -propenylene- $\alpha\gamma$ -diammonium salt and  $\text{Na}, \text{Na}, \text{Na}$ -trimethyl- $\text{N}\gamma, \text{N}\gamma, \text{N}\gamma$ -methyldiethyl- $\Delta\alpha$ -propenylene- $\alpha\gamma$ -diammonium salt in the presence of 0.1 N sodium isopropoxide and 0.1 N aqueous alkali. They found that when either of the ammonium salts was reacted with cold solutions of the alkali the  $\text{Na}, \text{Na}, \text{Na}$ -methyldiethyl- $\text{N}\gamma, \text{N}\gamma, \text{N}\gamma$ -triethyl- $\Delta\gamma$ -propenylene- $\alpha\gamma$ -diammonium salt was obtained in a 10-14 per cent yield while the isomer,  $\text{Na}, \text{Na}, \text{Na}$ -triethyl- $\text{N}\gamma, \text{N}\gamma, \text{N}\gamma$ -methyldiethyl- $\Delta\alpha$ -propenylene- $\alpha\gamma$ -diammonium salt was obtained in 40-48 per cent yield. The mixture isomers were analyzed by their difference in solubility since they had the same melting point.

Rothstein<sup>16</sup> studied the interconversion of  $\alpha$ -benzylsulphonyl- $\gamma$ -ethylsulphonyl- $\Delta\alpha$ - and - $\Delta\beta$ -propene. He found that these compounds were easily converted by heating to the melting point or by boiling with a solvent. The per cent of conversion to the  $\Delta\beta$ -isomer as was determined by the melting point of the mixture was 31.5 to 45 per cent.

Rothstein<sup>17</sup> also studied the interconversion of allyltrimethyl-

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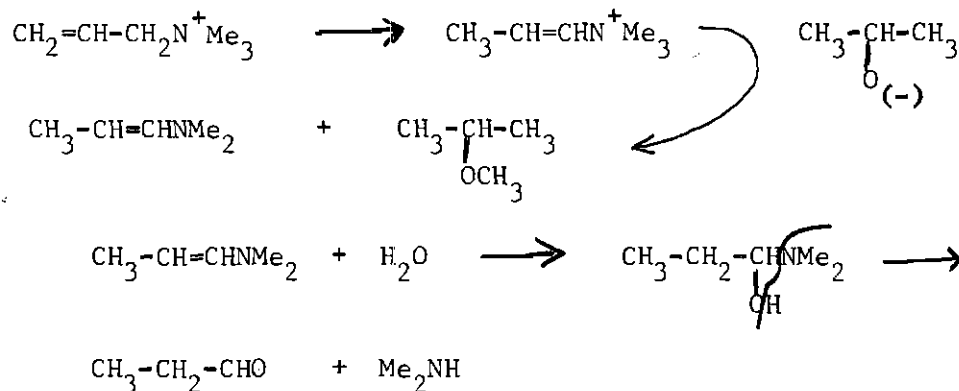
14. W. H. Watanabe and L. E. Conlon, J. Am. Chem. Soc., **79**, 2828 (1957).

15. C. K. Ingold and E. Rothstein, J. Chem. Soc., 1666 (1931).

16. E. Rothstein, J. Chem. Soc., 309 (1937).

17. E. Rothstein, ibid., 1560 (1940).

ammonium halide to its isomer propenyltrimethylammonium halide. The propenyltrimethylammonium halide was synthesized in order to have a sample of each compound in order to check the products of the inter-conversion reactions. When allyltrimethylammonium halide was heated with boiling sodium methoxide it was recovered unchanged. It would be recovered unchanged after heating to 45° for 12 hours in 0.5 N sodium isopropoxide. However prolonged action of this reagent at this temperature or higher temperatures led to the formation of dimethylamine. While Rothstein concluded that the two quaternary salts were not interconverted by alkoxide solution, a possible explanation which occurs to the present author for the formation of dimethylamine is shown in the following equations:



It seems likely that isomerization did take place in the allyltrimethylammonium halide which then loses a methyl group. If any water is present in the reaction mixture, it will add to the double bond giving a hydroxyl group adjacent to the amine nitrogen. The resulting compound is unstable and decomposes to give propionaldehyde and dimethylamine.

Reactions of Cyclopropyl Compounds.---The reactions of cyclopropyl compounds have not been studied very extensively. As a result, the mechanism for the reactions of these compounds has not been elucidated for many reactions. Some of the reactions proceed by a free radical, some by a carbanion, while the carbonium ion mechanism is postulated for certain reactions.

Lanpher, Redman, and Morton<sup>18</sup> found that the reaction of cyclopropane with amylsodium in absence of alkoxide ion gave cyclopropyl carbanion which, when carbonated, gave cyclopropanecarboxylic acid. This reactions shows that cyclopropane is more acidic than pentane. Hart and Sandri<sup>19</sup> reacted cyclopropyl chloride with lithium powder in pentane to give a mixture which gave products expected from cyclopropyl lithium. Carbonation of the mixture at  $-70^{\circ}$  gave cyclopropanecarboxylic acid while reaction with ketones gave tertiary alcohols. The mixture did not absorb ethylene even with ether present. Zimmerman and Thyagarajan<sup>20</sup> studied the reaction of phenylcyclopropyl sulfone with phenylsodium, lithium, and potassium. They observed that the cyclopropyl compound forms a carbanion intermediate during reaction. They also found that the acidity  $K_a$  of the cyclopropyl compound is only 40 to 80 per cent greater than that for the isopropyl compound. Walborsky and Hornyak<sup>21</sup> studied optically active

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18. E. J. Lanpher, L. M. Redman, and A. A. Morton, J. Org. Chem., **23**, 1370 (1958).

19. H. Hart and J. M. Sandri, Chem. and Ind., 1014 (1956).

20. H. E. Zimmerman and B. S. Thyagarajan, J. Am. Chem. Soc., **82**, 2505 (1960).

21. H. M. Walborsky and F. M. Hornyak, J. Am. Chem. Soc., **77**, 6022 (1955).

2,2-diphenylcyclopropylcyanide and showed by their experiments on this compound that the cyclopropyl carbanion is incapable of retaining its steric configuration. When 2,2-diphenylcyclopropanecarboxylic acid was treated with lithium di-isopropylamide, at room temperature, complete racemization occurred in less than 15 seconds. Lowering of the temperature did not prevent complete loss of optical activity.

In contrast, reaction of optically active 1-methyl-2,2-diphenylcyclopropyl bromide with butyllithium gave almost 100 per cent retention of configuration in the resultant 1-methyl-2,2-diphenylcyclopropyl-lithium. Reaction of the same bromide with magnesium metal gave largely racemization with some retention in the resultant Grignard reagent. Walborsky and co-workers have concluded that the reaction with magnesium metal probably proceeds by way of the corresponding cyclopropyl free radical which largely racemizes before conversion into the configurationally stable Grignard reagent.<sup>21b</sup>

Schuster and Roberts<sup>22</sup> found that the cyclopropyl radical is obtained in the decarbonylation of various aldehydes at 175-200°. The cyclopropyl radical has a large energy barrier compared to the cyclopropyl carbonium ion which prevents the isomerization of the cyclopropyl radical into the allyl radical. Hass and Schechter<sup>23</sup> found that the nitration of cyclopropane goes by a free radical process.

---

21. (b) H. M. Walborsky and F. J. Impastato, J. Am. Chem. Soc., **81**, 5836 (1959); H. M. Walborsky and A. E. Young, ibid., **83**, 2595 (1961); H. M. Walborsky, Chemistry Seminar, Georgia Institute of Technology, 1962.

22. D. I. Schuster and J. D. Roberts, J. Org. Chem., **27**, 51 (1962).

23. H. B. Hass and H. Schechter, J. Am. Chem. Soc., **75**, 1382 (1953).

They observed that nitrocyclopropane is much less acidic than the 2-nitropropane such that no ionization of nitrocyclopropane occurs in strong bases.

Skell and Starer<sup>24</sup> studied the de-oxidation of *n*-propyl alcohol. They postulated the *n*-propyl carbonium ion as an intermediate, and propylene and cyclopropane were obtained among the reaction products. Nitrous acid deamination of *n*-propylamine in aqueous solution also yields cyclopropane and propylene. They believe that the protonated cyclopropanes are not only an intermediate in the route to cyclopropanes, but may also be the intermediate in the major pathways leading to rearranged carbonium ions.

It is our hope that by studying the reaction of cyclopropyltrimethylammonium iodide in liquid ammonia we might be able to shed some light on the mechanism by which the salt is cleaved. The mechanism proposed by Grovenstein and co-workers<sup>6</sup> for cleavage of secondary alkyl groups would lead one to postulate the cleavage as taking place as a free radical. The reactions that will be run on this compound should give a possible answer to this question.

---

24. P. S. Skell and I. Starer, J. Am. Chem. Soc., **82**, 2971 (1960).

## CHAPTER II

## REAGENTS, SOLVENT, AND COMPOUNDS USED

Acetic Acid.--Baker reagent grade acetic acid was used without further purification.

Acetone.--Commercial grade acetone was purified according to the method of Conant and Kirner.<sup>25</sup> One liter of acetone was refluxed 24 hours with 120 grams of calcium oxide and 40 grams of potassium permanganate and was distilled through a Claisen head. The product has a boiling point of 56° at 738 mm.

Allyl Alcohol.--Matheson, Coleman, and Bell grade was dried over potassium carbonate and then distilled through a short Vigreux column. The alcohol had a boiling point of 92-93° at 738 mm.

Allyl-1-C<sup>14</sup> Alcohol.--Both Isotope Specialties and Volk radioactive allyl alcohol was distilled after dilution through a gold-plated spinning band column. The compound had a boiling point of 95° at 738 mm.

Allyl Chloride.--Columbia Organic Chemicals Company allyl chloride was distilled through a vacuum-jacketed glass-helices-packed column and had a boiling point of 45° at 738 mm.

Allyltrimethylammonium Chloride.--The compound was made by Chandra.<sup>26</sup> It was purified by recrystallization from *t*-butyl alcohol.

---

25. J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

26. S. Chandra, Ph. D. Thesis, Georgia Institute of Technology, 1961, p. 60



Purity was checked by Volhard titration for halides as given by Kolthoff and Sandell.<sup>27</sup>

Ammonia.--Matheson Company, Inc., anhydrous ammonia (99.9 per cent min. purity) was used without further purification.

Ammonium Chloride.--Baker reagent grade was used without further purification.

Carbon Dioxide.--Matheson Company, Inc., bone-dry grade (99.8 per cent min. purity) was used without further purification.

Chloroform.--Mallinckrodt U. S. grade was used without any purification.

1-Chloro-2-propanol.--Eastman Organic Chemical practical grade was used after distillation through a Claisen head and collecting portion boiling at 126-127°.

3-Chloropropyltrimethylammonium Chloride.--This compound was prepared by Chandra<sup>28</sup> and was purified by recrystallization from *t*-butyl alcohol. The purity was checked by a Volhard titration according to the method of Kolthoff and Sandell<sup>27</sup>. Anal. Calcd. for  $C_6H_{15}NCl_2$ : Cl, 20.65; Found: Cl, 20.32, 20.21, and 20.27.

*t*-Butyl Alcohol.--Matheson, Coleman, and Bell grade was used after refluxing and distilling from sodium.

Cyclopropane.--Matheson, Company, Inc., C. P. grade (99.0 per cent

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27. I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, Third Edition, the Macmillian Company, New York, N. Y., 545 (1961).

28. S. Chandra, op. cit., p. 62.

min. purity) was used without further purification.

Cyclopropyltrimethylammonium Iodide.--K and K Laboratories lot #17226 was recrystallized from t-butyl alcohol. The purity was checked by the Volhard titration of Kolthoff and Sandell.<sup>27</sup> Anal. Calcd. for  $C_6H_{14}NI$ : I, 55.90; Found: I, 54.77, 54.56, and 55.37.

5,5-Dimethyl-1,3-cyclohexanedione Methone.--Eastman white label grade was used without further purification.

Ethanol.--U. S. Industrial Chemical Co. commercial absolute ethanol was used without further purification.

Ethanol, 95 per cent.--U. S. Industrial Chemical Co. commercial grade 95 per cent ethanol was used without further purification.

Formic Acid.--Baker reagent grade formic acid was used without further purification.

Helium.--Marks Oxygen Co. helium was used as purchased.

Hydrogen Peroxide.--Baker analyzed reagent grade was used without further purification.

Iodine.--Baker reagent grade was used without further purification.

Lead Dioxide.--Baker reagent grade was used as purchased.

1,5-Hexadiene Biallyl.--Columbia Organic Chemical Company biallyl was used without further purification.

Methane.--Phillips research grade 99.5% pure was used without further purification.

1-Methyl-1-cyclopentene.--Aldrich Chemical Co., Inc., product was used without further purification.

Oxygen.--Marks commercial grade oxygen was used without further purification.

Phosphoric Acid.--Merck phosphoric acid 85 per cent was used as purchased.

Potassium.--Baker purified grade was used without further purification.

Potassium Dichromate.--Merck analyzed reagent grade was used without further purification.

Potassium Iodate.--Merck reagent grade was used without further purification.

Potassium Iodide.--Baker analyzed reagent grade was used without further purification.

Potassium Thiocyanate. Baker analyzed reagent grade was used without further purification.

Propane.--Matheson Company, Inc., C. P. grade (99.0 per cent min. purity) was used without further purification.

Propylene.--Matheson Company, Inc., C. P. grade (99.0 per cent min. purity) was used without further purification.

Silver Nitrate.--Baker analyzed reagent grade was used without further purification.

Sodium.--Baker purified sodium was used as purchased.

Sodium Hydroxide.--Baker analyzed reagent grade was used without further purification.

Stannous Chloride.--Baker reagent grade was used without further purification.

Sulfuric Acid, Fuming.--Baker technical grade was used with no further purification.

Thionyl Chloride.--Baker purified thionyl chloride was refluxed with sulfur for 4 1/2 hours and distilled twice through a three foot glass-helices-packed column at 95.5° and 739.2 mm. according to the method of Cottle.<sup>29</sup>

Tri-n-butyl Amine.--Eastman white label grade was stored over potassium carbonate for two days. It was then distilled through a Claisen head at a boiling point of 208° at 738 mm.

Trimethyl Amine.--Eastman Kodak anhydrous trimethyl amine was used without further purification.

Zinc.--Baker reagent grade powdered zinc was used without further purification.

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29. D. L. Cottle, J. Am. Chem. Soc., 68, 1380 (1946).

## CHAPTER III

## SYNTHESES

Propenyltrimethylammonium Chloride.--The preparation of propenyltrimethylammonium chloride was started according to the method of Rothstein.<sup>17</sup> To an acetone solution (142 ml.) containing 56.2 grams (0.951 moles) of trimethylamine was added 74.8 grams (0.792 moles) of 1-chloro-2-propanol. The reaction was allowed to proceed at room temperature for 25 days. At the end of this time, the solvent and excess amine was removed on a rotating evaporator. The sticky residue was then dissolved in hot ethanol and the mixture filtered through charcoal to remove colored impurities. The alcohol was evaporated at steam bath temperature and the residue was redissolved in a small portion of ethanol and an equal volume of dry ether was added. The salt, 2-hydroxypropyltrimethylammonium chloride, precipitated out and was collected. The yield was 18.2 grams or 15.1 per cent.

The salt was added to i-butyl alcohol and the mixture heated until the salt went into solution. The mixture was allowed to cool and the salt crystallized out of the alcohol. The salt after collection and drying amounted to 13 grams or 10.7 per cent.

The 13 grams of 2-hydroxypropyltrimethylammonium chloride was dissolved in 75 ml. of chloroform and treated with 26.0 grams of phosphorus pentachloride. The mixture was refluxed for 20 minutes. An equal volume of ether was added and the flask set aside to cool. A dark oil

settled out of solution. It would not crystallize so ethanol was added to take it back into solution and then the ethanol-ether mixture was evaporated. However, the salt would still not crystallize. The ether-ethanol was changed once per day for three days and still it would not crystallize. It was stoppered and left for 150 days before it crystallized out of solution. At this time it was filtered to give 1.8 grams (1.5 per cent yield) of 2-chropropyltrimethylammonium chloride. This product was treated with 20 ml. of 0.15 N KOH in ethanol. The workup to obtain the final product was never completed.

Allyl-1-C<sup>14</sup> Chloride.--The allyl-1-C<sup>14</sup> chloride was prepared from allyl-1-C<sup>14</sup> alcohol by the method of Young and co-workers.<sup>30</sup> The reaction was carried out in a 250 ml. three-necked flat bottomed flask containing a magnetic stirrer and fitted with a dropping funnel, a thermometer, and two receiving flasks in series. Into the flask was placed 30.53 grams (0.165 moles) of tri-*n*-butylamine, 9.58 grams (0.165 moles) of allyl-1-C<sup>14</sup> alcohol, and 30 ml. of di-*n*-butyl ether. The reaction flask was cooled in an ice-salt bath while 20 grams (0.165 moles) of thionyl chloride was added dropwise from the dropping funnel. The first of the receiving flasks was cooled with an ice-salt bath, the second with dry ice-acetone bath. Connected to the second receiver was a dry ice-acetone cold trap of the type used on vacuum pumps.

After all the thionyl chloride had been added, the ice-salt bath was removed and the mixture stirred for one hour at room temper-

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30. S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak, and W. G. Young, J. Am. Chem. Soc., **80**, 5965 (1958).

ature. Then the low-boiling fractions were removed by distillation at 150-160 mm. for 20 minutes at room temperature. The flask was heated in an oil bath until the temperature of the vapors reached 80°. The liquids collected in the two receivers were mixed and shaken with 5 ml. of 5 per cent sodium bicarbonate solution. The upper organic layer was washed with ice-cold water. In the meanwhile, the liquid collected in the large trap was shaken with a 10 per cent solution of sodium carbonate until the solution remained basic to litmus paper. The organic layer was then washed with ice-cold water. The two layers were dried over Drierite to remove any water and then distilled through a small micro distillation apparatus until the vapor reached 21° at 150-160 mm. During this run the allyl chloride was diluted with 1 ml. of non-radioactive allyl chloride. The yield of allyl-1-C<sup>14</sup> chloride was 62.5 per cent based on the amount of alcohol used.

Allyl-1-C<sup>14</sup>-trimethylammonium Chloride.--To 100 ml. of anhydrous acetone that had been kept at dry ice-acetone temperature for two hours was added 20 ml. of anhydrous trimethylamine that had been chilled with an ice-salt bath. The allyl-1-C<sup>14</sup> chloride, 2.75 ml. or 34.22 mmoles, was added and the solution kept at the dry ice-acetone temperature for six hours. It was then placed in a refrigerator for forty-eight hours. The mixture was removed from the refrigerator and allowed to stand at room temperature for two hours. Then 130 ml. of dry ether was added and the mixture shaken. After standing for 24 hours the crystalline product was separated by filtration and amounted to 4.01 grams or 87 per cent based on the allyl-1-C<sup>14</sup> chloride used.

## CHAPTER IV

## EXPERIMENTAL TECHNIQUES AND PROCEDURES

Gas-handling Technique. --The gas-handling apparatus described by Rogers<sup>31</sup> was used in the preparation of gas samples. This consisted of a horizontal manifold with four stopcocks joined to it at right angles, three of which had ball joints for connections, and a ball joint on each end for a gas reservoir and mercury manometer. To the first stopcock was connected the helium tank while to the last stopcock was connected a gas cylinder containing a suitable hydrocarbon. The second stopcock was used to connect the gas bulb in preparing the sample and the vacuum pump was connected to the third stopcock. There was a one-meter glass tube that dipped into a reservoir of mercury so the rubber tubes connecting the cylinders could be swept out before introducing any gas into the manifold.

The level of mercury in the gas sample bulb and gas reservoir was lowered until it was only one-half inch deep in the bulb and then the rubber hose to the mercury reservoir was pinched off with a screw clamp. The bulbs were then connected to the manifold and the stopcock to the pump was opened. The complete system was evacuated to 0.1 mm. or less and then filled with the gas being used. It was alternately filled and evacuated three times. After the third evacuation, the gas was allowed to enter the system until a certain pressure, depending on the gas,

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31. L. C. Rogers, M. S. Thesis, Georgia Institute of Technology, 1962, p. 33



was obtained. In every case, the pressure had to be large enough to read with precision (100 mm. or more). After having read and recorded the pressure, the stopcocks to the reservoir and the gas bulb were both closed and the manifold was again evacuated and flushed with helium for three times. After the third time, helium was allowed to flow into the manifold until it flowed out the exit tubes. The stopcocks were then cracked, one at a time, to allow helium to flow into the bulbs until the gas was at atmospheric pressure. The pressure was again read and recorded and the bulb removed to be taken to be analyzed by vapor phase chromatography.

After having been analyzed, the bulb was connected to the system and the stopcock opened. The bulb was evacuated along with the manifold to 0.1 mm. or less. The vacuum pump was closed off and then the gas reservoir was opened to the system. The pressure was read and recorded and then the two bulbs were closed off. The manifold was evacuated and flushed with helium three times. The bulbs were again brought up to atmospheric pressure with helium and the pressure recorded. The bulb was then removed and taken to be analyzed again. This time the gas of interest was found at a lower pressure. This procedure was repeated until a pressure of hydrocarbon of 0.001 mm. was reached.

Gas Chromatography.--The gas chromatography was carried out on a Perkin-Elmer Vapor Fractometer, Model 154-C and 154-D, that were equipped with a Precision Gas Sampler. The Precision Gas Sampler has sample tubes that hold one-fourth, one, five, and twenty-five milliliters of gas. In most of this work, the one milliliter and occasional-

ly the five milliliter sample tube was used for gas measurements. Helium was used as the carrier gas in all the experiments.

While propane, propylene, cyclopropane, and biallyl along with the different isomers of biallyl had to be determined on Perkin-Elmer Column "E" containing dimethylsulfolane (2,4-dimethyltetrahydrothiophene-1,1-dioxide), the methane was determined on Perkin-Elmer Column "J" that contained silical gel. These columns are two meters long and 6.25 mm. in diameter. Both of these columns were operated at a temperature of 32-34° while the pressures varied from 5 psi to 15 psi. The sensitivity used ranged from one for some of the biallyl isomers to 256 for the cyclopropane and other gases.

When the work on the vapor fractometer was started, it was decided to make calibration curves for each of the product gases and the biallyl. The curves were made by running various partial pressures of the components and then making plots of the peak heights versus the pressure of the component. These partial pressures ran from 0.01 mm. for methane up to 758 mm. for other gases, with as many as three curves being obtained between this range of pressures.

It was soon discovered that these curves would not be accurate for more than a short time. This is because the machines vary from day to day in their characteristics as well as that the curves for one machine were different from the curves of the other machine.

The samples were then analyzed by first running a single point to find out the difference between that point as obtained that day and the value obtained from the curve. This correction factor was then added to or subtracted from the heights obtained that day to give the value

for the partial pressure. The values obtained from this method were found to be in error. A new method of determining the correct value was tried.

This method consisted of running a calibration curve for each gas each day that the gases were analyzed. This would assure us of the machine having the same characteristics for both the unknown and known. In order to use this method of correcting and obtaining the true value for the partial pressure, it was assumed that the calibration curve for the gases is a straight line over the range of partial pressures required to bracket the unknown gas. This would give an accurate pressure because of the two known pressures being so close to the unknown. This method seemed to give very good results.

It was found that the temperature of the machine caused a variation in the times required for each material to show up as a peak on the chart paper. However, it was also found that by increasing the pressure one could decrease the time required for each component to show up as a peak. When the pressure was increased from 5 psi to 15 psi, the time was reduced from three or four minutes to something less than one minute for propylene. Also, biallyl came off in 11 minutes at the higher pressure as compared to 30 minutes at the lower pressure. This increase in pressure was necessary in order to be able to see the different compounds that are present in the biallyl mixture. Even at this higher pressure, some of the isomers of biallyl did not appear for 30 to 35 minutes. At this length of time, the isomers that appeared were just "bumps". In other words, the peaks were so long in coming off that they appeared as very broad peaks. This result made quantitative work very difficult.

It was found that the faster a component came over on the column, the sharper and more defined was the peak as shown on the recorder chart. This sharpness was helpful in that it gave a definite point to measure for the peak height. It was also for this reason that the change to higher pressure was made for biiallyl and isomers of biiallyl.

The Precision Gas Samples valve has two positions. The first position permits the sample of gas to flow through the valve and sample tube into the vacuum pump which was used to evacuate the sample tube. The second position allowed the helium to flow through the sample tube sweeping the sample into the machine and through the sample detector and column.

It should be pointed out here that the present vapor fractometer works on the principle of a difference in thermal conductivity. This difference is detected by a set of matched thermistors. Helium is flowing constantly across one of the thermistors. Across the other thermistor is flowing helium which comes through the column in the machine. When a sample is introduced into the machine, it is swept through the column by the carrier gas. When the helium containing the sample flows over the thermistor, it has a different thermal conductivity from pure helium because of the presence of the sample being analyzed. This difference in conductivity is then fed into the amplifier in the recorder where the signal is amplified. This amplification is recorded on the chart paper in the form of a peak. The substance is then swept out of the machine through the gas exit tube.

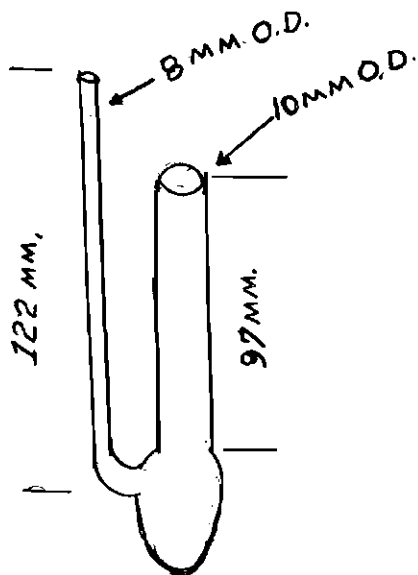
The sample tube along with the valve is evacuated by the vacuum pump. The bulb described in the gas handling technique is connected to

the valve. When the system has been evacuated from the stopcock on the gas bulb to the stopcock on the pump, the stopcock to the pump is closed to shut off the pump. Then the stopcock to the gas bulb is opened and the valve and sample tube are allowed to fill up. The level of the mercury in the reservoir is raised to the level of mercury in the gas bulb in order for the pressure on the valve and sample tube to be equal to the atmospheric pressure. Then the stopcock is closed and the sample tube and valve are full of the gas to be analyzed. This operation is carried out with the valve in position one. The stopcock to the pump is opened and the system is again evacuated. This process is carried out two times to make sure that all air is out of the sample tube. The third time the valve is turned to position two which introduces the sample into the vapor fractometer. This method was used for all gases as well as biallyl and biallyl isomers.

The method just described is known as an analytical process. However, the vapor fractometer was also used in another way. This other way is known as a preparative process. In this case, the compound prepared was the biallyl obtained from the liquid ammonia reactions of allyl chloride with sodium. The machine was equipped with a large preparative column, Column "E", which is 3 meters long and 25 mm. in diameter. The column was placed in the machine in the same manner as any other column. The machine was run at the temperature of 32-34°C but the pressure used was all that could be obtained on the machine, in excess of 30 psi. The sample (0.5 ml.) was introduced into the machine through a rubber septum with a hyperdermic syringe. The different

isomers of biallyl were separated according to their differences in retention times (or the time to pass through the machine).

The sample of biallyl that was wanted was collected by the use of a long slender hyperdermic needle which was connected to the gas exit tube. The needle was inserted into a small collection bulb of the type shown below. Two of these bulbs were connected with a rubber tube between the longer sides. They were inserted into a half pint Dewar flask filled with dry ice-acetone which permitted the condensation of the biallyl. The needle reached almost to the bottom of the bulb, which held 5-7 milliliters, while the neck of the needle formed a tight seal against the side of the larger tube. This forced the helium to flow out through the second bulb while the biallyl was condensed in the first bulb. The biallyl was recovered in an amount equal to 90 per cent of the amount inserted into the machine. The sample that was collected was then ready to be taken and ozonized for the next step in the series of operations.



Ozonolysis.--The procedure employed in this process is essentially the same as described by Chandra<sup>32</sup> with a few exceptions. The machine used to generate ozone was a Wesbalch Model T-23, a commercial machine for producing ozone. The machine was found to be producing one millimole of ozone per minute as determined by the titration of  $I_2$  liberated from a  $KI-KH_2PO_4$  solution using thiosulfate as titrant and starch solution as indicator.

The ozonizer was cooled with water. When a good stream of water was flowing through the generator, the oxygen was turned on. The oxygen regulator on the tank was set at 25 psi while the regulator on the machine was set at 7 psi. The flowmeter on the machine was set at 0.015. The machine was then turned on with the voltage set initially at zero. The voltage was then turned up slowly to 120 volts, the increase taking approximately five minutes. When the correct voltage was reached, the oxygen-ozone was then passed through the chloroform solution containing the compound that was to be reacted with the ozone at  $-60^\circ$ . The ozone was passed through the solution until the reaction was complete, the completeness being shown by the chloroform solution turning blue from the absorption of ozone in the chloroform and from the terminal solution of  $KI-KH_2PO_4$  turning dark brown showing the liberation of free iodine. The oxygen was allowed to flow through the machine for twenty minutes while the ozone left in the machine was being swept out.

The glass equipment used in the ozonization was the same as used by Chandra.<sup>32</sup> The only change was the amount of chloroform used

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32. Chandra, op. cit., pp. 83-86.

for the solvent. Sixty milliliters of chloroform was used for solid and liquid compounds while 40 additional milliliters was used in another tube hooked in series for gases. The tubes were placed in beakers containing acetone-dry ice at  $-60 \pm 5^\circ$ . To the last tube was connected a tube containing the  $\text{KI-KH}_2\text{PO}_4$  solution as an indicator to tell when free ozone was passing through the solution, the indicator also acting as a reducing agent to reduce the ozone to oxygen.

The chloroform solution of the ozone and ozonide was then added to a flask containing 2 grams of powdered zinc and a glass-enclosed magnetic bar which was turning rapidly. To the rapidly stirring solution was then added three milliliters of glacial acetic acid along with a volume of water equal to the volume of chloroform used. The mixture was allowed to react at room temperature for thirty minutes. At the end of this time, the mixture was filtered to remove any unreacted zinc that might be present in the mixture. The solution contained formaldehyde and acetaldehyde or succinaldehyde, depending on what was ozonized. To the water-chloroform mixture containing the aldehydes was added 25 milliliters of ethanol which contained five to seven grams of dimethone (5,5-dimethyl-1,3-cyclohexanedione). The mixture was allowed to stand in a refrigerator overnight.

The next day the mixture was removed from the refrigerator and the chloroform evaporated by using a steam bath. After evaporation of the chloroform, the hot solution was set aside to cool. The dimethone derivatives of the aldehydes precipitated out upon cooling. They were collected and dried in the drying pistol under vacuum at  $56^\circ$ . The



solution was then set aside and left for two or three days because it was discovered that the acetaldehyde derivative did not come out of solution when the formaldehyde derivative precipitated. However, upon standing, the acetaldehyde derivative came out in very good yields and relatively pure state. This is something that was discovered quite by accident and resulted in better total yields.

After drying the solid derivatives, the combined derivatives of formaldehyde and acetaldehyde were dissolved in ten milliliters of glacial acetic acid. This acid solution was heated on the steam bath for six hours and then left standing overnight. The next day ten to fifteen milliliters of water was added to the solution which was then set aside for one to two hours. The derivatives of the aldehydes precipitated when water was added to the acid solution. The derivatives were collected and dried. They were then dissolved in twenty milliliters of chloroform. The chloroform solution was poured into a 100 milliliter separatory funnel and extracted four times, each with 20 milliliters of 4 per cent sodium hydroxide solution. After the fourth extraction, the chloroform solution was washed with cold water and the cold water added to the sodium hydroxide solution. The chloroform solution was poured into an evaporating dish and the chloroform evaporated on the steam bath. The solid product left in the dish was the dimethone derivative of the acetaldehyde which had been converted into the anhydride.

The basic solution obtained from extraction of the chloroform contained the sodium salt of the dimethone derivative of formaldehyde. The basic solution was neutralized with two normal hydrochloric acid.

Upon neutralization, the formaldehyde derivative precipitated. The precipitate was collected and dried. After drying, it was recrystallized from 95 per cent ethanol three times. The formaldehyde dimethone derivative had a melting point of 189-190°. The acetaldehyde derivative was also recrystallized from the ethanol the same number of times, and had a melting point of 176-177°.

The work-up just described was used for nearly all the ozonizations. However, one basic change was tried on the ozonide of the bi-allyl. In this case, the chloroform solution was divided into two equal volumes. One of the portions was worked up to obtain the formaldehyde derivative by the use of zinc reduction while the other half of the chloroform solution was worked up according to the method used by Bailey.<sup>33</sup> All the chloroform was evaporated from the ozonide by use of a rotating evaporator and a good vacuum pump at room temperature. When all the solvent had been stripped off, all that was left was a thick syrupy liquid that should have been the pure ozonide. To this ozonide was added fifteen milliliters of 90 per cent formic acid and 8 milliliters of 30 per cent hydrogen peroxide. The solution was then refluxed for thirty minutes and left standing overnight. The next day the volatile compounds were removed from the succinic acid by use of a rotating evaporator and water aspirator. The acid was collected and placed in a vacuum apparatus where it was vacuum sublimed. The acid was then recrystallized from water one time and dried. It was now ready to be used in radioactive analysis. The acid had a melting point of

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33. P. S. Bailey, *J. Org. Chem.*, 22, 1548 (1957).

188-189°.

Analyses for Radioactivity.--The analyses for radioactivity were carried out by using the combustion apparatus adapted by Chandra<sup>34</sup> from the design of Ropp.<sup>35</sup> The combustion reagents were prepared according to the procedure of Van Slyke and co-workers.<sup>36</sup> The solid combustion reagent was prepared by mixing two parts by weight of potassium iodate and one part potassium dichromate. The liquid combustion reagent was prepared by mixing 33 milliliters of syrupy phosphoric acid with 67 milliliters of fuming sulfuric acid. This solution was then heated with one gram of potassium iodate at 160-190° until the iodate had dissolved.

The sample being combusted was weighed out in a platinum boat using a Metler microbalance, the usual amount of compound ranging from five to fifteen milligrams. The boat was placed in the reaction chamber and the chamber attached securely to the system with the aid of small springs. Bone-dry carbon dioxide was swept through the combustion train for ten to fifteen minutes. This was to sweep all the air out of the system so there would not be anything but carbon dioxide in the system.

While the sweeping of the system was being carried out, the cell that is to be used for the collection of carbon dioxide was evacuated.

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34. S. Chandra, op. cit., pp. 86-89

35. G. A. Ropp, personal communication to Dr. E. Grovenstein, Jr.

36. D. D. Van Slyke, J. Plazin, and J. R. Weisiger, J. Biol. Chem., 191, 299 (1951).

It was pumped out and flushed three times with carbon dioxide, and finally evacuated, closed off, and placed in the combustion train to complete the combustion system.

The acid reagent was poured into the holder, the quantity being from seven to nine milliliters. The stopcock on the cell was opened to the system to create a slight vacuum in the system. Then the stopcock to the acid was opened to allow the acid to flow into the reaction chamber. The acid was stopped just before the acid chamber was empty in order to prevent air from getting into the system. The reactants were allowed to stand for approximately seven minutes to permit combustion to take place at room temperature. Then the acid was heated slowly with a micro burner until dense white fumes of sulfur trioxide were observed. The heating was then stopped and the stopcock to the carbon dioxide line was opened to permit carbon dioxide to bubble through the hot acid solution. This was continued until the ionization chamber was brought to atmospheric pressure with carbon dioxide.

The cell was then removed from the system and carried to the instrument room where it was connected to the vibrating reed electrometer (Applied Physics Corporation, Model 31). Here a direct voltage of 135 volts was connected across the outside of the cell and the electrometer head. The negative pole of the battery was attached to the cell while the positive pole was attached to the electrometer head. This permits the electrons that are given up to flow to the center of the head where they are measured by one of two methods, either the rate of drift method or the steady deflection method. All of the results

reported in this thesis will be by the rate of drift method. Some calculations of specific activity are given by Chandra.<sup>37</sup> In the present work a standard sample of benzoic acid-C<sup>14</sup> (supplied by Chem. Trace Corporation, Cambridge, Mass.) was used to calibrate the cell.

Allyl alcohol for analysis was weighed out in a very thin-walled bulb and then the bulbs were sealed off. The bulb was placed in the reaction chamber along with a glass-enclosed magnetic bar. After the acid had been added, the magnetic bar was used to break the the glass bulb and thereby permit the allyl alcohol to come in contact with the acid reagent.

The allyltrimethylammonium chloride was weighed out in very small glass-stoppered weighing bottles, dried for three days at 56° in the Abderhalden to make sure that the compound was dry, and then reweighed to obtain the correct weight of compound. One of the small weighing bottles containing the compound was then placed in the reaction chamber and the solid combustion agent poured on to it. The acid was added and the combustion carried out as described previously.

Reactions of 3-Chloropropyltrimethylammonium Chloride with Sodium in Liquid Ammonia.--The reactions of 3-chloropropyltrimethylammonium chloride were carried out in the liquid ammonia apparatus constructed by Rogers.<sup>38</sup> The system was assembled and swept with gaseous ammonia for fifteen minutes, the exit ammonia being absorbed in water spraying into an ammonia trap. A dry ice-acetone bath was then placed around

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37. S. Chandra, op. cit., pp. 133-135.

38. L. C. Rogers, op. cit., pp. 28-31.

salt were collected in the top of the brine bulb. After the last of the gases had been swept from the reaction vessel, the bases were transferred to a gas burette containing saturated brine that was one normal in hydrochloric acid. Here the gases were measured and then passed back and forth into an Orsat gas washer to remove any ammonia or amines that might be present. The volume was again measured and the washing continued until a constant volume was reached. This volume was then recorded along with the temperature and barometric pressure. The gases were then transferred to a gas sample bulb that could be removed from the ammonia system and taken to the instrument room where the gases were analyzed by the Perkin-Elmer Vapor Phase Chromatograph as described previously. The yields and products are given in Table 4.

Reactions of Cyclopropyltrimethylammonium Iodide with Sodium in Liquid Ammonia.--The apparatus used and the procedure employed in this series of reactions were the same as described on page 34. The salt was recrystallized from *n*-butyl alcohol and then dried. After drying, the purity was checked by a Volhard titration. The ammonia was condensed and allowed to warm to its boiling point. The salt and sodium were weighed out and then placed in the system.

In some reactions the salt was first added to the ammonia and allowed to dissolve. It was found to be soluble in the liquid ammonia. The sodium was then added and the reaction allowed to go to completion. In each run, the ammonia turned blue and remained dark blue until all the ammonia had evaporated. The amount of ammonia used in this series of reactions was  $50 \pm 5$  milliliters.

In half of the runs, the mode of addition of the salt and sodium were reversed, i.e., the sodium was first dissolved in the liquid ammonia and then the quaternary salt was added. This reversal was made to see if the concentration of sodium atoms present in the liquid ammonia had any influence on the nature of the products and the yields of products. In each run the ratio of the cyclopropane to methane was determined. The yields and products for each run are summarized in Table 5.

Reactions of Allyltrimethylammonium Chloride with Sodium in Liquid Ammonia.--The general procedure and apparatus described on page 34 were used for these reactions. The allyltrimethylammonium chloride was found to be extremely hygroscopic in nature. For this reason the salt had to be dried in vacuum for two days at 56° before using. The salt was found to be completely soluble in ammonia at the boiling point of liquid ammonia.

In this series of liquid ammonia reactions both modes of addition were tried. The initial two runs were carried out by first adding the salt to the liquid ammonia and then the sodium while the rest of the runs were made by adding the sodium to the liquid ammonia and then the salt. These methods of addition were employed to check whether or not the concentration of sodium had any effect on the nature or amount of products.

These reactions were carried out in  $100 \pm 5$  milliliters of ammonia except where noted otherwise in Table 6. In this reaction, biallyl and isomers of biallyl were produced in varying amounts. The

the reaction chamber to condense the gaseous ammonia. The time for condensation varied from 15 to 30 minutes, depending on the amount of ammonia required in the reaction. All of the reactions of 3-chloropropyltrimethylammonium chloride were carried out using  $70 \pm 5$  milliliters of liquid ammonia at  $-33^\circ$ , the boiling point of liquid ammonia.

The cooling bath was removed and the ammonia was allowed to warm up to the boiling point with constant stirring by a glass-enclosed magnetic bar. When the boiling point was reached the quaternary salt was weighed out, placed in a retort and attached to the system. The sodium was divided into ten to 12 pieces for addition to each liquid ammonia run. The sodium was then placed in the retort that had just been removed from the system and was then replaced on the system. If ammonium chloride was being used, it was also placed in a retort at this time and attached to the system. The apparatus was now swept with ammonia obtained from the boiling ammonia to remove air brought into the system with the retorts. In all the reactions of 3-chloropropyltrimethylammonium chloride, the sodium was then added to the liquid ammonia solution containing the quaternary salt. The ammonia remained blue after the addition of sodium until all the ammonia had evaporated.

The ammonia upon evaporation was absorbed in a saturated brine solution in a large collection bulb. As the brine became saturated with ammonia, the brine solution was replaced with a fresh solution. The necessity of changing the brine at the right time to prevent the loss of reaction products required constant attention. The brine solution was changed three to four times per reaction.

The gases that were obtained from the cleavage of the ammonium



yield of biallyl and isomers of biallyl were determined by v.p.c. in every run except one. The yields of biallyl and isomers were necessary along with the yields of propylene and methane in order to obtain a number to represent the relative ratio of cleavage of allyl versus methyl group by sodium.

Isomerization of Allyl-1-C<sup>14</sup>-trimethylammonium Chloride with Potassium Amide in Liquid Ammonia.--The apparatus of Fernelius and Johnson,<sup>39</sup> used by Stevenson<sup>40</sup> and Rogers,<sup>41</sup> was modified greatly for use in these runs. It is shown schematically in Figure 1.

The allyl-1-C<sup>14</sup>-trimethylammonium chloride when used in liquid ammonia reactions was dried in vacuo at 56° and 0.05 mm. for three days to remove any water since the compound is extremely hygroscopic. The compound (1.44 grams or 10.6 mmoles) was dried and weighed in retort 2. Since the per cent yield was not to be determined, the absolute weight was not determined by reweighing the empty retort after addition to the liquid ammonia.

The ammonia was passed through the tube containing barium oxide to remove any water present in the ammonia. The ammonia is passed through the first stopcock and passed into a trap to absorb the ammonia by spraying water. The stopcock is turned and the ammonia is then allowed to pass through trap A, reaction vessel B, trap C, and mercury

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39. W. C. Fernelius and W. C. Johnson, J. Chem. Educ., **6**, 441 (1929)

40. Stevenson, op. cit., pp. 73-117.

41. Rogers, op. cit., pp. 28-31.

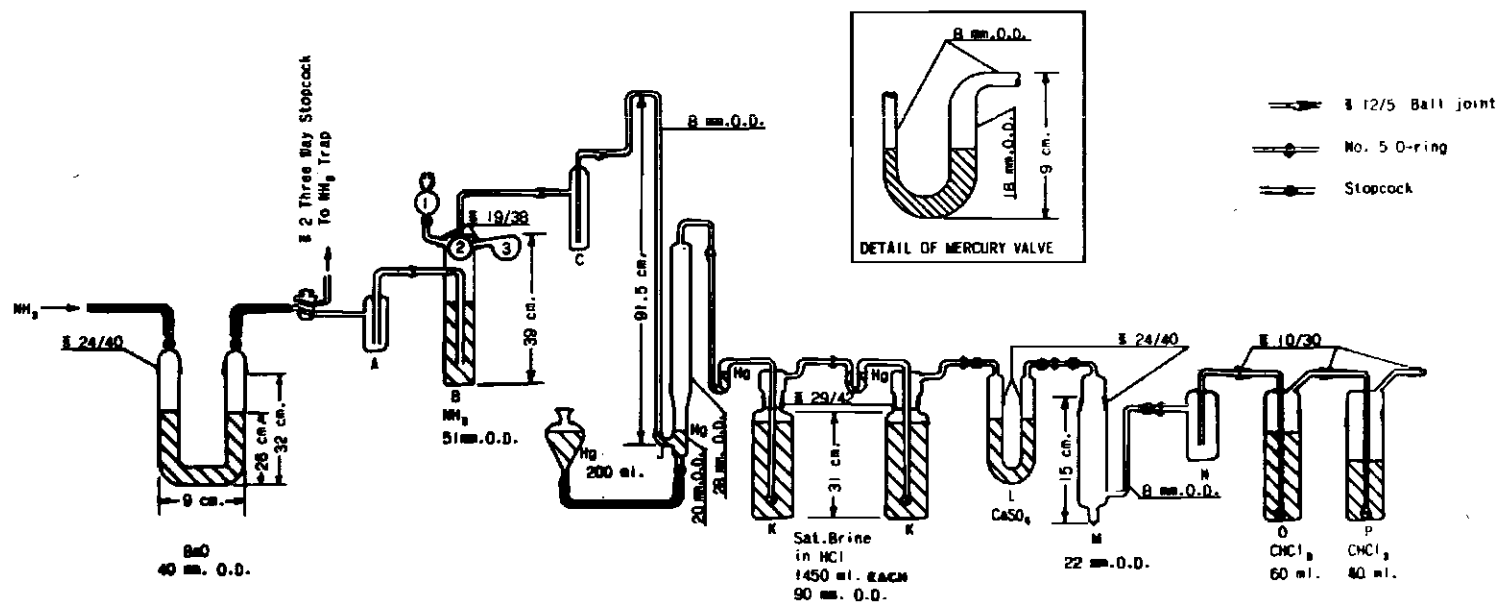


FIGURE 1. LIQUID AMMONIA APPARATUS FOR RADIOACTIVE MATERIALS

value K, and out ball joint Q for 15 minutes to remove any traces of air present in the system. After this time, the reaction vessel was immersed in a dry ice-acetone bath to condense the ammonia. The condensation of the ammonia causes the level of the mercury in valve K to rise in tube D. The ammonia was condensed until  $105 \pm 5$  ml. had been collected. The ammonia was then allowed to reach the boiling point.

While the ammonia was reaching the boiling point, the potassium metal (0.176 grams or 4.55 mg. atoms) was weighed out in the ratio of two moles of salt to one mole of potassium. The reason was so not all the allyltrimethylammonium chloride could be isomerized to 1-butenyl-dimethylamine or (1-methyl-2-propenyl)dimethylamine. The potassium was then placed in the retort, the retort put back into the system, and the system swept with gaseous ammonia obtained from the boiling ammonia in the reaction system. The ammonia was then cooled down to just below its boiling point with a liquid ammonia bath. The potassium was added to the liquid ammonia. The ammonia turned dark blue upon the addition of potassium. The solution was allowed to stand for 8 hours. At the end of this time, the potassium had turned to potassium amide.

The ammonia solution was again allowed to warm to its boiling point. While the ammonia was warming up, the sodium was weighed in a small weighing bottle under mineral oil. Also the ammonium chloride was weighed out. After the ammonia started boiling the retorts 2 and 3 were removed from the system and the sodium (0.40 grams or 17.45 mg. atoms) placed in retort 2 and the ammonium chloride (0.26 grams or 4.90 mmoles) in retort 3. The retort of allyl-1- $C^{14}$ -trimethylammonium

chloride was removed from the drying pistol and attached to the reaction system. After all the retorts were attached, the apparatus was swept with gaseous ammonia. The reaction vessel was then cooled with ethanol-dry ice to  $-72^{\circ}$  since this was the temperature at which the reactions were to be run.

In the meantime, the rest of the system was put together. The ammonia traps labeled K were each filled with 1450 ml. of saturated brine that was in hydrochloric acid. The trap L was filled with Drierite to dry the gases coming out of the ammonia traps. The traps M and N did not contain anything at the present time. The trap Q contained 60 ml. of chloroform and trap P contained 40 ml. of chloroform.

The last half of the system was then connected to the ball joint Q and the reaction was ready to be started. The salt was added to the ammonia and the potassium amide. The reaction was allowed to go for 27 minutes. After this time ammonium chloride was added to destroy the potassium amide.

After destroying the potassium amide, the sodium was added to the salt solution to cleave the ammonium salt. The dry ice-ethanol bath was kept around the reaction vessel for thirty minutes after the addition of sodium. The cooling bath was removed and the ammonia allowed to warm up to the boiling point again while stirring with a magnetic bar. As the ammonia evaporated, it was absorbed in the brine-HCl solution. When the ammonia started evaporating a dry ice-acetone trap was placed around trap M, Q, and P. The traps Q and P were used to dissolve

any gases from the reaction and to hold them until they could be ozonized. The trap M was used to collect the biallyl that is formed in the reaction.

As soon as the liquid ammonia had evaporated, a four-liter beaker was placed around B, K, and L. In these beakers was placed water which was then heated until the temperature of the container and contents had reached the temperature of 65-70°. This was done to make sure that the biallyl formed in the reaction could be swept out of the reaction system and into the trap that was designed for this purpose. Around the trap M was placed a half-pint Dewar flask that contained liquid nitrogen. This liquid nitrogen was cold enough to cause all the biallyl to condense out as the helium swept it from the reaction system. The system was swept with 10-15 liters of helium to remove all reaction products. The traps Q and P were cooled to  $-60^{\circ} \pm 5^{\circ}$  to dissolve all propylene formed in the reaction in order that this gas might be ozonized.

After the system was swept out, the trap M was left in the liquid nitrogen while the traps Q and P were removed and taken to be ozonized. The results are given in Tables 3 and 7.

Reactions of Allyl Chloride with Sodium in Liquid Ammonia.--The reactions of allyl chloride with sodium were carried out in the same apparatus described on page 37. The ammonia was condensed in the reaction vessel and then allowed to warm up to the boiling point. At this time the sodium was placed in a retort and ammonium chloride in another retort, if ammonium chloride was to be used. Also the ammonia was allowed to evaporate until  $100 \pm 5$  ml. of ammonia remained in the reaction vessel and any air was finally removed during this evaporation.

The ammonia was again cooled, this time with a dry ice-ethanol bath to  $-70^{\circ} \pm 5^{\circ}$ .

The allyl chloride was placed in a special dropping funnel that was fitted to the reaction vessel. The allyl chloride was measured out and put in the funnel, 4 milliliters being used in the reaction. The stopcock was opened and the allyl chloride was introduced into the ammonia. After stirring a few minutes the sodium was added to complete the reaction taking about 5 minutes to complete the addition of sodium. After 20 minutes, ammonium chloride was added to the ammonia to destroy sodium amide and any excess sodium. The ammonia was then allowed to evaporate.

The collection procedure for the biallyl is the same as described for the isomerization of allyl-1-C<sup>14</sup>-trimethylammonium chloride. The biallyl was then taken and analyzed by v.p.c. to determine the number of isomers present along with the yield of each isomer.

The yields were calculated on the basis of the biallyl curves, assuming that the isomers give the same peak heights according to concentration as does biallyl. The yields calculated by this method are given in Table 8. However, it had been discovered that the best method to use in determining the concentration of isomers is the peak area. A calculation was made on the curves obtained from the biallyl from the allyltrimethylammonium chloride. It was found that isomer I was an average of  $31.8 \pm 3.24$  per cent lower by the peak height method while isomer II was found to be only  $15.06 \pm 5.52$  per cent lower by the peak height method. The peak area method assumes that the area under the

peak is proportional to the amount of compound present and that the constant of proportionality is the same for all the bialllyl isomers as for bialllyl itself. Since the curves for the bialllyl obtained from the allyl chloride have been thrown away, it can only be stated that the yields given in the table for allyl chloride are very likely to be in error for compounds both above and below bialllyl in retention time. How much in error the yields are is not known. One run was analyzed by both methods and the results are given in Table VIII.

Reactions of Allyl-1-C<sup>14</sup> Chloride with Sodium in Liquid Ammonia.--

The procedure employed in these reactions was described on page 37. The apparatus was the same as used in the isomerization reaction. The quantity of allyl-1-C<sup>14</sup> chloride used was only about half that employed in the non-radioactive runs. The same general conditions were used. Each run of the radioactive material used ammonium chloride to destroy sodium amide and excess sodium after 25 minutes. This was to prevent the sodium or sodium amide from isomerizing the products. The bath was removed and the ammonia allowed to evaporate.

The bialllyl was collected in the same manner as the non-radioactive material. However, the bialllyl was here taken and put into the preparative column of the v.p.c. where the bialllyl was separated from the isomers of bialllyl and then osonized. The results are given in Tables 1 and 2.

In run I, 1.85 ml. (22.68 mmoles) of allyl-1-C<sup>14</sup> chloride was added to 100 ml. of liquid ammonia at -70° and then 1.1945 grams (51.9 mg. atoms) of sodium was added in some 8 to 10 pieces over a period of

5 minutes. After completion of the addition of the sodium, the mixture was allowed to stand for 25 minutes before addition of 2.6324 grams (49.2 mmoles) of ammonium chloride. After the usual work-up of the reaction mixture, somehow ozonization of the chloroform solution of the propylene failed to give any formaldehyde or acetaldehyde derivatives. Some 0.9 ml. (or 0.63 grams) of crude biallyl was obtained. After purification of the biallyl on the preparative vapor phase chromatography apparatus, ozonolysis and then the usual work-up some 0.0722 grams of crude succinic acid was obtained; however, for unknown reasons no formaldehyde derivative was obtained. The succinic acid was purified by vacuum sublimation and recrystallization from water. The sample used for radioactivity assays had m.p. of 188-189° range.

The allyl chloride used in run I was prepared by addition of 0.4 ml. of non-radioactive allyl chloride to an unmeasured volume of radioactive allyl chloride or molar activity of 0.2947 microcuries per millimole (as measured on a sample of allyl-1-C<sup>14</sup>-trimethylammonium chloride prepared, without dilution from this sample of allyl chloride). After removal of the 1.85 ml. sample of diluted allyl chloride for run I there remained a volume of allyl chloride which was estimated visually to measure 0.3 ml. (lower possible estimate 0.2 ml., upper estimate 0.6 ml.) Ozonization of the remaining allyl chloride gave a crude weight of formaldehyde and acetaldehyde dimethone derivatives of 967 mg.; this weight agrees with expectations for ozonization of 0.3 ml. of allyl chloride (a known sample of 0.5 ml. of allyl chloride gave 1.7764 grams of the crude dimethone derivatives). From these data it may be calculated that



1.65 to 2.05 ml. of the radioactive allyl-1-C<sup>14</sup> chloride was diluted with 0.4 ml. of non-radioactive allyl chloride. Radiochemical assays of the formaldehyde derivative derived from ozonization of allyl chloride proceeded satisfactorily; however, the three assays made on the corresponding acetaldehyde derivative gave very poor agreement with each other and further analyses were impossible because of exhaustion of the sample. Further details concerning run I are recorded in Table 1.

To run II, the quantities of reagents used were 2.2 ml. (27.1 mmoles) of allyl chloride and 1.141 grams (49.5 mg. atoms) of sodium. The reaction was allowed to proceed for 25 minutes and then 2.80 grams (54.2 mmoles) of ammonium chloride was added to destroy the sodium amide and sodium. This run was carried out exactly like run I. The ozonization of reactants and products in this run proceeded satisfactorily. From biallyl there was obtained dimethone derivatives of formaldehyde (m.p. 187-188°) and succinic acid (m.p. 188-189°) which were assayed for their radioactivity. For further details concerning this run see Table 2.

TABLE 1

Reaction of Allyl-1-C<sup>14</sup> Chloride with Sodium in Liquid Ammonia

Run I

Compound	Specific Activity (microcuries/mole) x10 <sup>4</sup>
Formaldehyde from the Allyl Chloride	78 ± 1 75 ± 1 <hr/> Av. 76 ± 2
Acetaldehyde Anhydride from the Allyl Chloride	1647 ± 12 1400 ± 9 1922 ± 32 <sup>a</sup> <hr/> Av. 1656 ± 177
Succinic Acid from Biallyl	3633 ± 5 3655 ± 27 <hr/> Av. 3644 ± 16
Allyl-1-C <sup>14</sup> -trimethyl Ammonium Chloride	2938 ± 1 2957 ± 12 <hr/> Av. 2946 ± 9
Calcd. for Allyl-1-C <sup>14</sup> Chloride	2425 ± 45

<sup>a</sup>This sample of acetaldehyde derivative was redried before this analysis.

TABLE 2

Reaction of Allyl-1-C<sup>14</sup> Chloride with Sodium in Liquid Ammonia

Run II

Compound	Specific Activity (microcuries/mmmole) $\times 10^4$
Allyl-1-C <sup>14</sup> Alcohol	(3276 $\pm$ 14) <sup>a</sup> (3538 $\pm$ 9) 3886 $\pm$ 8 3700 $\pm$ 4 3750 $\pm$ 5 3869 $\pm$ 14 3828 $\pm$ 10 (3606 $\pm$ 16) <hr/> Av. 3807 $\pm$ 65
Succinic Acid from Biallyl	4954 $\pm$ 24 4980 $\pm$ 24 4928 $\pm$ 11 5118 $\pm$ 18 4750 $\pm$ 23 <sup>b</sup> <hr/> Av. 4946 $\pm$ 85
Formalldimethone from Ozonization of Biallyl	1400 $\pm$ 12 (1280 $\pm$ 11) 1442 $\pm$ 12 1462 $\pm$ 12 1374 $\pm$ 14 1424 $\pm$ 9 1400 $\pm$ 23 <hr/> Av. 1417 $\pm$ 27
Acetaldimethone Anhydride from Ozonization of the Propylene Obtained by Reaction of Allyl Chloride with Sodium	1844 $\pm$ 14 1900 $\pm$ 11 1795 $\pm$ 12 1783 $\pm$ 16 (1682 $\pm$ 4) 1812 $\pm$ 32 1818 $\pm$ 1 <hr/> Av. 1825 $\pm$ 31

Formaldehyde from Ozonization of the  
Propylene Obtained by Reaction of Allyl  
Chloride with Sodium

(1743  $\pm$  14)  
1857  $\pm$  16  
1879  $\pm$  21  
1856  $\pm$  16  
1869  $\pm$  12  
1884  $\pm$  11  
1854  $\pm$  1  

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Av. 1866  $\pm$  13

Formaldehyde from Ozonization of  
Allyl-1-C<sup>14</sup> Chloride

47  $\pm$  1  
50  $\pm$  1  
43  $\pm$  4  
44  $\pm$  1  
43  $\pm$  3  

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Av. 45  $\pm$  2

<sup>a</sup>The figures in parentheses represent the numbers left out of the average values as given in this table.

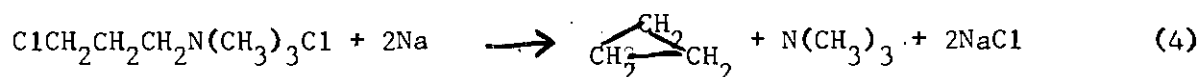
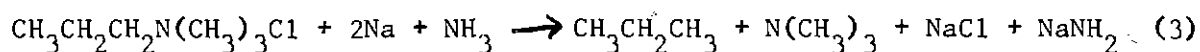
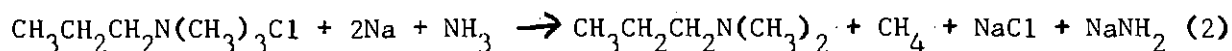
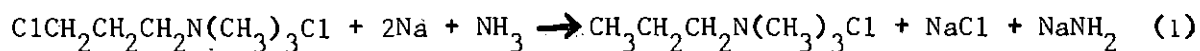
<sup>b</sup>This sample of succinic acid was vacuum sublimed and redried before analyzing. The other samples were sublimed only one time before analyzing.

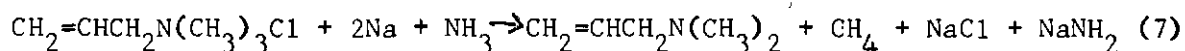
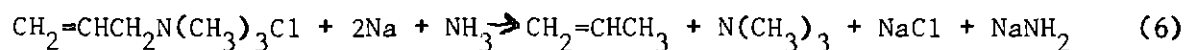
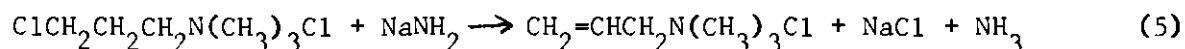
## CHAPTER V

## RESULTS AND DISCUSSION

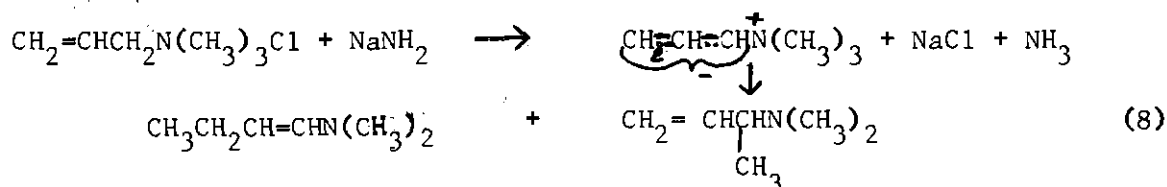
The present work consisted of a study of the reactions with sodium in liquid ammonia of allyltrimethylammonium chloride, cyclopropyltrimethylammonium iodide, 3-chloropropyltrimethylammonium chloride, allyl chloride, and allyl-1-C<sup>14</sup> chloride. In addition a study was made of the isomerization of allyl-1-C<sup>14</sup>-trimethylammonium chloride with potassium amide in liquid ammonia. The compounds were synthesized by known reactions. Radioactive reactions were first carried out using non-radioactive compounds to make sure that the reactions could be run in good yield.

3-Chloropropyltrimethylammonium Chloride.--The cleavage of 3-chloropropyltrimethylammonium chloride was carried out by solution of the quaternary salt in liquid ammonia followed by addition of small pieces of metallic sodium. The hydrocarbon products which have been identified from this reaction are summarized in Table 4. These products can be accounted for qualitatively by the following reactions:

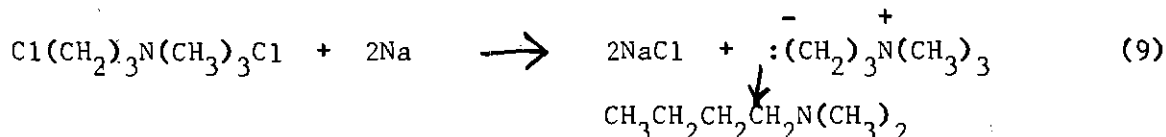




The total yield of hydrocarbon products reported in Table IV is highly variable, ranging from 12.7 to 82.2 per cent. While in some cases the low yields are possibly to be attributed to mechanical losses of gaseous products, such mechanical losses are deemed unlikely since in an apparatus similar to the present almost quantitative yields of hydrocarbons have been obtained<sup>6</sup> in cleavages of tetraalkylammonium halides. A more likely cause is conversion of the quaternary ammonium salt to tertiary amines which were not analyzed for in the present work. Thus a likely reaction is a Steven's rearrangement upon allyltrimethylammonium ion:



Rearrangements of this type have recently been reported by Hellmann and Scheytt.<sup>42</sup> Another possibility is the related rearrangement:



42. H. Hellmann and G. M. Scheytt, Ann., 654, 39 (1962).

TABLE III

REACTIONS OF 3-CHLOROPROPYLTRIMETHYLAMMONIUM CHLORIDE WITH SODIUM IN LIQUID AMMONIA<sup>a</sup>

Salt <sup>b</sup> mmole	Sodium mmole	Propylene	Propane Yield of	Methane Products,% <sup>c</sup>	Cyclopropane	Total	100 x PrH/CH <sub>4</sub>
0.757	1.52	4.0 ± 0.4	1.87 ± 0.15	73.7 ± 1.1		79.6	2.5
0.895	1.36 <sup>d</sup>	9.5 ± 0.8	0.35 ± 0.04	17.25 ± 0.7	0.12 ± 0.01	27.3	2.0
0.802	4.07	17.6 ± 0.5	0.24 ± 0.01	40.6 ± 1.0	0.25 ± 0.01	58.7	0.59
0.897	4.22	3.4 ± 0.4	0.122 ± 0.01	9.2 ± 0.9		12.7	1.3
1.09	5.74	34.3 ± 0.5	0.034 ± 0.003	46.3 ± 1.2	1.60 ± 0.08	82.2	0.07
0.76	3.87	19.1 ± 0.6	0.04 ± 0.01	52.7 ± 1.6	0.4 ± 0.1	72.2	0.08

<sup>a</sup>These reactions were carried out in 70 ± 5 milliliters of ammonia at -33°

<sup>b</sup>The quaternary salt was dissolved in the ammonia and then the sodium added to the solution.

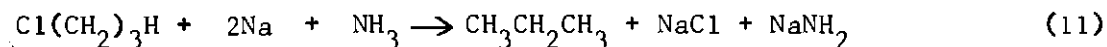
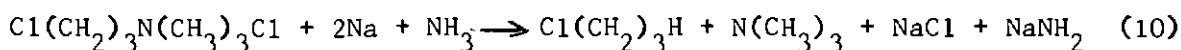
<sup>c</sup>The yields are based on the amount of quaternary salt unless otherwise stated.

<sup>d</sup>The yields are based on sodium since it is the limiting reagent in this reaction.

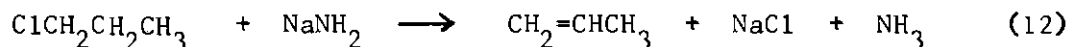
<sup>e</sup>The ± numbers indicate the accuracy of the determination of the yield with regard to the reproducibility of the v.p.c. machine for each substance analyzed.

Since reactions (5) and (8) are homogeneous while the remainder of the reactions are partially heterogeneous the yields and relative amounts of products might be expected to vary in a sporadic fashion from run to run because of variability in rate of stirring, size of sodium particles, and other factors which affect the rate of solution and ultimately rate of reaction of the sodium.

Another peculiarity in the present results is that the ratio of propane to methane is highly variable. On the basis of the reactions (2), (3), and (7) this would not be expected since reaction (7) should be very unimportant (see the section on cleavage of allyltrimethylammonium chloride in the present thesis) and therefore the ratio of propane to methane should be governed by the ease of cleavage of propyl and methyl groups from propyltrimethylammonium ion. This ratio times 100, however, has been reported<sup>6</sup> to be  $0.58 \pm 0.06$ . In the present work a highly variable value was obtained. A possible explanation is that propane in the present case is formed also by another path, conceivably by the process:

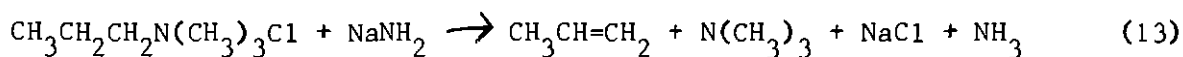


The n-propyl chloride produced by reaction (10) could then serve as an alternative source of propylene through the homogeneous reaction (12) which competes with the partially heterogeneous process (11):



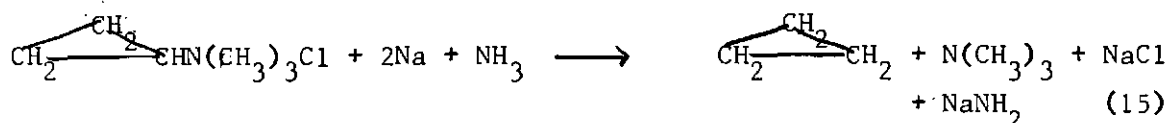
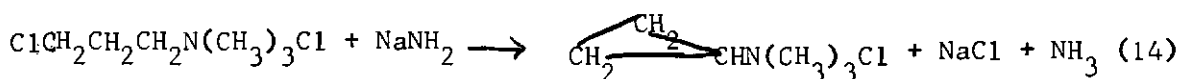


An alternative source of propylene is provided by reaction (13):



In fact, however, it has been found<sup>6</sup> that cleavage of *n*-propyltrimethylammonium iodide by sodium in liquid ammonia gives only 1 to 2 per cent of propylene and, therefore, this reaction is unlikely to be the major source of propylene in the present work.

While cyclopropane formation may be accounted for qualitatively by reaction (4) which may be regarded mechanistically as proceeding by an initial cleave of either a C-Cl or a C-N bond, followed by  $\beta$ -elimination for  $\text{N}(\text{CH}_3)_3$  or  $\text{Cl}^-$  respectively, yet if this were the only mode of cyclopropane formation the yield of cyclopropane might be expected to parallel the yield of methane (since the parallel reaction (1) yields *n*-propyltrimethylammonium ion which on further reaction gives predominantly methane<sup>6</sup>). Table 3, however, reveals a poor correlation between the yield of methane and cyclopropane but a better correlation between the yield of propylene and that of cyclopropane. If the latter correlation is valid, then cyclopropane formation evidently involves a reaction with sodium amide like the important reactions (5) and possibly (12) which have been suggested to lead (ultimately) to propylene. A likely reaction path appears to be the following:



Cyclopropyltrimethylammonium iodide has, in fact, been found (see later discussion) by experiment to give mostly cyclopropane on cleavage by addition of sodium metal to a liquid ammonia solution of the salt.

While initially it was planned to investigate, by use of carbon-14 labeling, the origin of the soluble bond in the propylene produced by reaction of 3-chloropropyltrimethylammonium ion with sodium, the extraordinary complexity of the reaction, as revealed by the present preliminary study, discouraged such a course of action and attention was turned toward a detailed study of the more elementary reaction (6), (7), and (15) together with a parallel study on reactions of allyl chloride with sodium.

Cyclopropyltrimethylammonium Iodide.--This quaternary salt was not very hygroscopic and therefore was easy to handle without special precautions. Moreover the salt was completely soluble in liquid ammonia at the concentrations studied in the present work. Reaction with sodium was carried out by two modes of addition. In the first mode, sodium metal, cut in some ten or more pieces, was added portionwise to the solution of quaternary salt in liquid ammonia. Addition of sodium metal was complete in some three minutes. In the second mode, the crystalline quaternary salt was sprinkled slowly into the deep-blue solution of sodium in liquid ammonia over a period of about five minutes. The addition of solids was effected by suitable rotation and tapping upon the glass retort containing sodium metal or pulverized quaternary salt. The results from six reactions are recorded in Table 5. The hydrocarbon

products consisted of cyclopropane and methane. Propylene and propane were looked for in the first run; the amount present was 0.12 per cent propane and 0.019 per cent propylene.

The ratio of cyclopropane to methane formed by the first mode of addition was rather irregular; however the ratio was always higher by the first mode of addition than by the second, even when about the same quantities of reactants were used. The ratio of cyclopropane to methane formed by the second mode of addition decreased regularly as the concentration of sodium metal increased. Since the effective concentration of sodium metal in the first mode of addition is likely lower than the corresponding concentration in the second mode of addition all the results in Table 5 are summarized by the conclusion that the ratio of cyclopropane to methane decreases as the concentration of sodium in the liquid ammonia solution increases. Because of the heterogeneous nature of the present reactions a more exact statement concerning the variation of this ratio with the concentration of sodium cannot be made. In the reactions in which small pieces of sodium metal were added to the liquid ammonia solution of the quaternary salt, the surface of the sodium metal became dark blue but the surrounding solution (at any appreciable distance from the surface of the sodium) remained colorless until all or nearly all of the quaternary salt had reacted; therefore the reactions between sodium and the quaternary salt must be extremely fast and the rate is apparently governed by the rate of solution of the sodium metal (or in the inverse mode of addition by the rate of solution of the quaternary salt).

TABLE IV

REACTION OF CYCLOPROPYLTRIMETHYLAMMONIUM IODIDE  
WITH SODIUM IN LIQUID AMMONIA AT -33°

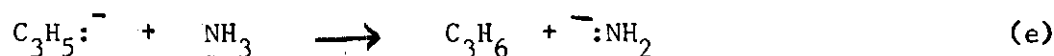
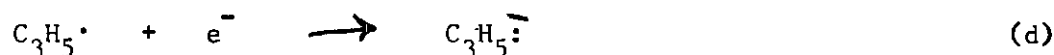
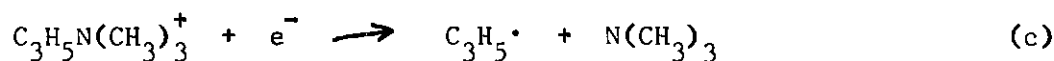
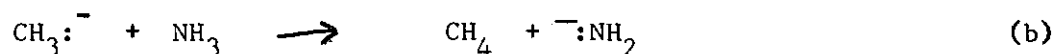
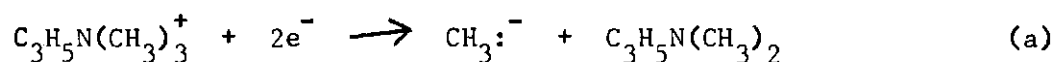
Sodium	Quaternary Salt	<u>Yield of Products, %</u>		Ratio
<u>mmoles</u>	<u>mmoles</u>	<u>Cyclopropane</u>	<u>Methane</u>	<u>C<sub>3</sub>H<sub>6</sub>/CH<sub>4</sub></u>
Sodium metal (solid) added to solution of quaternary salt in liquid ammonia:				
3.07	1.00	66.0 ± 0.7	12.0 ± 0.6	5.5 ± 0.3
5.00	1.07	16.0 ± 0.8 <sup>a</sup>	2.69 ± 0.3 <sup>a</sup>	6.0 ± 1.0
9.36	1.53	61.0 ± 1.2	15.6 ± 0.8	3.9 ± 0.3
Crystalline quaternary salt added to solution of sodium in liquid ammonia:				
6.86	1.27	46.8 ± 0.5	27.4 ± 0.8	1.71 ± 0.07
9.55	1.61	48.7 ± 1.0	30.7 ± 0.9	1.58 ± 0.08
21.2	1.52 <sup>b</sup>	39.1 ± 1.2	43.3 ± 0.5	0.90 <sup>b</sup> ± 0.03

<sup>a</sup>The products were diluted with air to an unknown extent before analysis, hence only the relative yields of cyclopropane and methane are of significance.

<sup>b</sup>In this run 65 ml. of liquid ammonia was used as solvent. In the other runs the volume of liquid ammonia was 50 ml.

<sup>c</sup>The ± numbers represents the reproducibility of the v.p.c. for each analysis.

The observed variation in the ratio of cyclopropane to methane with sodium concentration can be explained by the mechanism of Grovenstein and Stevenson.<sup>6</sup> According to these workers, the methyl group cleaves from quaternary nitrogen as a carbanion, while secondary alkyl groups such as isopropyl and s-butyl cleave as free radicals. By analogy with these simple secondary alkyl groups, the cyclopropyl group might be expected to cleave as a free radical.



If in such mechanisms the effective concentration of electrons can be equated with the stoichiometric concentration of sodium (Na), then the rate of cleavage of cyclopropyl and methyl groups is given by the equations:

$$d[\text{C}_3\text{H}_6]/dt = k_c(\text{Na})[\text{C}_3\text{H}_5\text{N}^+(\text{CH}_3)_3] \quad (\text{f})$$

$$d[\text{CH}_4]/dt = k_m(\text{Na})^2[\text{C}_3\text{H}_5\text{N}^+(\text{CH}_3)_3] \quad (\text{g})$$

where the symbols enclosed in brackets refer to the concentration of the species indicated and t is time. The ratio of cyclopropane to methane produced at any particular concentration of sodium is then given by the relation

$$d[C_3H_6]/d[CH_4] = (k_c/k_m)(Na)^{-1} \quad (h)$$

This equation is in at least qualitative accord with the experimental results.

Allyltrimethylammonium Chloride.--Allyltrimethylammonium chloride is extremely hygroscopic in nature. For this reason the compound was dried in vacuo for three days at 56° before using. The reactions were run in liquid ammonia, the volume ranging from 50 to 100 milliliters.

Allyltrimethylammonium chloride is extremely soluble in liquid ammonia. Because of this solubility, it was not necessary to wait any appreciable length of time before adding sodium in the runs in which the salt was first dissolved in the liquid ammonia.

The salt was cleaved in eight different reactions with the sodium to salt ratio ranging from 2.2 to 60. During these reactions the mode of addition was varied. The first two reactions were run with the sodium being added to the liquid ammonia while the remainder of the reactions were made with the salt being added to the liquid ammonia solution of sodium. It should be noted here that in either case, the reaction that resulted was very violent. At times it seemed as if the reaction system were going to be destroyed when the reactants were mixed.

Methane is presumed to cleave as a carbanion by a two-electron transfer as previously proposed.<sup>6</sup> The alkyl group may cleave either as a free radical (one electron transfer) or a carbanion (two-electron transfer). A distinction can be made between these two processes on the basis that the ratio of higher molecular-weight hydrocarbons

to methane for this reaction turns out to be the highest in the table.

The second of these experiments consisted of setting up the liquid ammonia reaction system and introducing a known volume of methane into the system. The ammonia was allowed to evaporate and the gases were collected and analyzed as usual. The amount of gases introduced into the system was 30 milliliters of a mixture of methane (0.442 mm.) and propylene (758.6 mm.). The quantity of methane introduced was  $7.07 \times 10^{-4}$  mmoles. When this is compared to the amount of methane obtained in the reactions of allyltrimethylammonium chloride (from  $5.2 \times 10^{-4}$  to  $11.3 \times 10^{-4}$  mmoles), it is seen that the amount introduced in the sample is comparable to that usually obtained from the sodium reactions. The amount that was recovered in the collected sample of gases was, within experimental error, the same amount as was introduced into the system. The quantity of propylene introduced into the system was 1.21 mmoles as compared to 0.97 to 1.74 mmoles in the sodium reaction. It is concluded, therefore, that the recovery of methane, even in the small quantities produced in the present reactions, was good.

During one of the reactions in which the salt was added first, a color change was noted when the sodium was added to the solution. The ammonia solution turned a slight yellow when the sodium was first added. The color then became darker and remained a dark yellow for a few minutes. After this length of time, the ammonia solution turned the characteristic dark blue color and remained blue until all the ammonia had evaporated. Hellmann and Scheytt<sup>42</sup> reported that when allyltriethylammonium bromide was reacted with sodium amide in liquid ammonia

TABLE V

REACTION OF ALLYLTRIMETHYLAMMONIUM CHLORIDE WITH SODIUM IN LIQUID AT  $-33^{\circ}$ 

Sodium mmoles	Quaternary Salt, mmoles	Yield of Products, <sup>b</sup> %					Molar ratio C <sub>3</sub> H <sub>6</sub> + C <sub>6</sub> H <sub>10</sub> CH <sub>4</sub>
		Propy- lene <sup>d</sup>	Methane	Biallyl <sup>e</sup>	Biallyl Isomer I	Biallyl Isomer II	
3.67 <sup>a</sup>	1.65	67.5	0.034	1.8	0.24		2050
4.90 <sup>a</sup>	2.11	65.4	0.029	1.51	0.46	0.14	2320
6.11 <sup>a</sup>	1.93	82.1	0.037				2220
7.16	1.30	74.6	0.046	1.09	0.15	0.04	1650
7.39 <sup>c</sup>	1.72	77.8	0.030	1.93	1.8	0.14	2680
20.7	2.00	73.5	(0.013)	1.53	0.46	0.14	(5820)
33.9	1.57	74.2	0.045	1.26	0.23	0.05	1681
140	2.35	73.9	0.048	2.73	0.12	0.03	1600
							Av. 2030 ± 320

<sup>a</sup>In this run the quaternary ammonium salt was dissolved in liquid ammonia and solid pieces of sodium were slowly added to the solution. In runs not marked by an asterisk, the sodium was first dissolved in liquid ammonia and then the solid quaternary ammonium salt was slowly added to the solution.

<sup>b</sup>The yields of biallyl and biallyl isomers are calculated on the basis that one mole of biallyl (or biallyl isomer) is produced per mole of allyltrimethylammonium chloride in order that the ratio of the combined percentage yields of propylene plus biallyl plus biallyl isomers to methane may represent the relative rate of cleavage of allyl versus methyl groups by sodium. The propylene has a likely error in reproducibility of one per cent, methane of 10 per cent and biallyl and isomers of 10 per cent.

<sup>c</sup>Reaction was run in 50 ml. of liquid ammonia. In other runs 100 ml. of liquid ammonia was used.

<sup>d</sup>The retention time of propylene as found on Perkin-Elmer Column "E" is 0.8 minutes at 15 psi and  $33^{\circ}$ . The retention times for biallyl and isomers of biallyl are given in Table VIII.

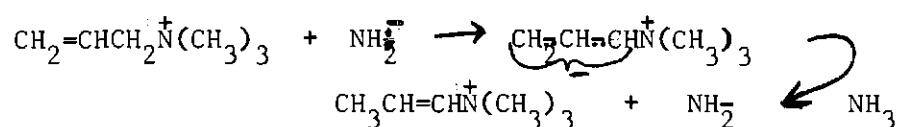
<sup>e</sup>The yields of biallyl and isomers are determined by the peak area method assuming that the area for each compound produces the same area per millimole.



a dark brown or red-violet color was obtained and this was attributed to the species  $\text{CH}_2=\text{CH}-\text{CH}_2\text{N}^+\text{Et}_3$ .

Isomerization of Allyl-1-C<sup>14</sup>-trimethylammonium Chloride.--There has been some question as to whether allyltrimethylammonium chloride could be isomerized to propenyltrimethylammonium chloride. Rothstein<sup>17</sup> stated that it was known that the allyl compound did not show any tendency to be isomerized; and since he synthesized the propenyl compound and found that it was stable to alkoxide ions, he concluded that the two compounds were not interconverted by alkoxide solution. However, it was thought that the allyltrimethylammonium chloride could be isomerized to the propenyl compound by stronger bases and with this in mind the following work was done.

On the basis of a suggestion by Chandra<sup>43</sup> it was thought that the isomerization could be carried out with amide ion according to the following equation:



Potassium amide would be the best amide since it is more soluble in ammonia than is sodium amide. Also potassium amide can be formed without the addition of a catalyst such as ferric nitrate. The presence of such a catalyst is undesirable since in subsequent cleavage of the quaternary salt by sodium the catalyst would cause much loss of sodium

43. Chandra, op. cit., p. 124.

TABLE VI

PER CENT OF ISOMERIZATION IN REACTIONS OF ALLYL-1-C<sup>14</sup> COMPOUNDS<sup>45</sup> IN  
 IN LIQUID AMMONIA AT -33°

Compound (mmoles)	Metal (mg.atoms)	Per Cent Isomeri- zation before re- action	Apparent Isotope Effect $k_{12}/k_{14}$	Calculated Isomerization %
AllylNMe <sub>3</sub> Cl 5.61	Na 14.2	1.23	1.072 ± 0.029	0.78
AllylNMeCl 5.46	Na 15.2	1.23	1.072 ± 0.015	0.78
AllylNMe <sub>3</sub> Cl 4.43	Li 25.7	1.23	1.135 ± 0.022 1.110 ± 0.010	1.85 Av.
p-Tolyl allyl sulfide 6.1	Na 15.2	3.82	1.113 ± 0.033	1.45
p-Tolyl allyl sulfide 6.1	Li 14.3	3.82	1.269 ± 0.021	8.91
p-Tolyl allyl sulfide 7.3	Li 15.7	3.82	1.098 ± 0.010	0.65

45. Chandra, op. cit., pp. 101-104.

<sup>a</sup>Ammonium sulfate was used in this reaction but is not soluble to any extent in liquid ammonia.

TABLE VII

ISOMERIZATION OF ALLYL-1-C<sup>14</sup>-TRIMETHYLAMMONIUM CHLORIDE

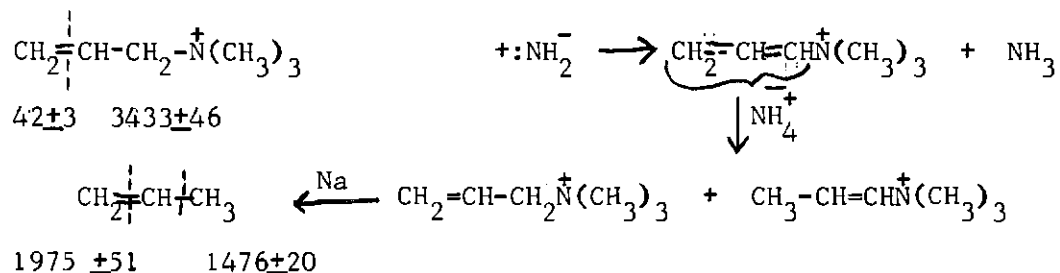
<u>Compound</u>	<u>Specific Activity in Microcuries per Millimole x 10<sup>4</sup></u>
Formaldehyde from Ozonization of Propylene	1999 ± 24 <sup>a</sup>
	1996 ± 13
	1983 ± 22
	1848 ± 2
	2054 ± 16
	Av. 1976 ± 51
Acetaldehydedimethone anhydride from Ozonization of Propylene	1427 ± 8
	1462 ± 13
	1493 ± 16
	1474 ± 45
	Av. 1476 ± 20
Formaldehyde from Ozonization of Allyl-1-C <sup>14</sup> -trimethylammonium Chloride	45 ± 1
	44 ± 1
	37 ± 2
	Av. 42 ± 3
Allyl-1-C <sup>14</sup> -trimethylammonium Chloride	3517 ± 28
	3433 ± 28
	Av. 3475 ± 43

<sup>a</sup>The numbers following the ± signs for each individual determination are the mean deviations from the average values recorded for each combustion. These numbers, therefore, indicate the reproducibility of the measurements made by the vibrating-reed electrometer. The average value for all the combustions made on each compound are also shown along with the mean deviation; the latter value reflects both errors made in the combustion technique and errors made in the counting technique.

by conversion of sodium to sodium amide.

The isomerization by potassium amide was carried out in liquid ammonia at  $-72^{\circ}$ . After the reaction had gone for 27 minutes ammonium chloride was added to destroy the potassium amide. Then sodium was added to cleave the allyltrimethylammonium chloride. The ammonia solution did not turn blue but yellow, then orange, and finally red. The latter color lasted until all the ammonia had evaporated. In this run there was added only enough sodium to reduce some 61 per cent of the quaternary salt.

Isomerization of allyl-1-C<sup>14</sup>-trimethylammonium chloride was ascertained by ozonization and assay of the resultant formaldehyde and acetaldehyde as their dimethone derivatives. The distribution of carbon-14 is summarized by the following equations where the numbers below each formula are the molar activities in microcuries per millimole times  $10^4$  for the portion of the molecule indicated.

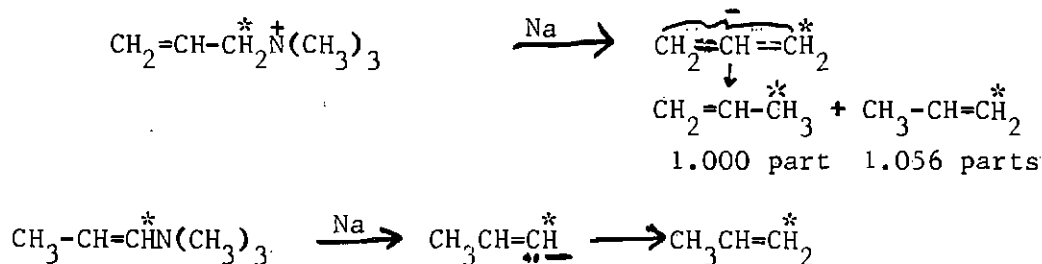


If it is assumed that protonation of allyl carbanion, formed by cleavage of allyltrimethylammonium ion by sodium in presence of acids such as ammonium chloride, gives propylene having 5.6% excess activity in its methylene group as reported by Chandra<sup>44</sup>, and further that propenyl

44. Chandra, op. cit., p. 118.

carbanion is formed and protonated without rearrangement, then it is possible to calculate the percentage of propylene resulting from cleavage of propenyltrimethylammonium ion as 12.3 per cent of the total. \*

These assumptions are summarized by the following equations:



The detailed calculations are given in Appendix B.

By applying similar calculations to the data reported by Chandra<sup>45</sup> for cleavage of various allyl-1-C<sup>14</sup> compounds by sodium or lithium in liquid ammonia in absence of added acids (save ammonium sulfate which is nearly insoluble in liquid ammonia), the apparent percentage isomerization can be calculated as shown in Table 6. The amount of isomerization so calculated is generally small but is occasionally large as in the cleavage of *p*-tolyl allyl sulfide with lithium. The variable extent of isomerization under such conditions may be due to different effective

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\* This calculation does not give the % isomerization of allyltrimethylammonium ion to propenyltrimethylammonium ion since enough sodium was present to cleave only about 61 per cent of the quaternary salt and since the propylene to methane ratio from propenyltrimethylammonium is unknown, considerable uncertainty exists as to the percentage isomerization to propenyltrimethylammonium ion

44. Chandra, op. cit., p. 118.

contact times between the allyl compound and amide ion; such differences may arise from the heterogeneous nature of the reactions and differing rates of mixing of reactants.

Reactions of Allyl Chloride and Allyl-1-C<sup>14</sup> Chloride.--Chandra<sup>45</sup>

found that allyl chloride reacts with sodium in liquid ammonia in the absence of ammonium chloride to give bialllyl as major olefin along with propylene and isomers of bialllyl. When ammonium chloride is present in the liquid ammonia solution, the yield of bialllyl and bialllyl isomers is greatly reduced and the yield of propylene is increased. These results suggest that bialllyl is produced by reaction of allyl carbanion with allyl chloride and that ammonium ion reduces the yield of bialllyl by rapid protonation of the allyl carbanion to give propylene. A major purpose of the present research was to investigate the mechanism of formation of bialllyl with aid of carbon-14 as a tracer.

Some preliminary experiments were run with non-radioactive allyl chloride under the same conditions that were to be used for radioactive allyl chloride with sodium in liquid ammonia. The results are given in Table 8.

The three most likely mechanisms for the reaction of sodium with allyl-1-C<sup>14</sup> chloride in liquid ammonia to give bialllyl seem to be the following:

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45. Chandra, op. cit., p. 106

TABLE VIII

REACTIONS OF ALLYL CHLORIDE WITH SODIUM IN LIQUID AMMONIA AT -72°

Allyl chloride (mmoles)	Sodium (mg.atoms)	Ammonium chloride <sup>a</sup> (mmoles)	Yield of bialllyl and isomers <sup>b</sup>	Distribution of products <sup>c</sup>						
				I	II	B	III	IV	V	VI VII
36.80	53.62	62.46	8.50 <sup>d</sup>	23.8	6.09	62.2	0.15	4.0	3.0	0.54
33.78	51.12	54.24	34.99	3.4	0.35	96.1	0.13			
45.00	65.6	68.84	69.33							
36.76	60.2	63.0	75.0	9.2	1.09	89.2		0.37	0.74	1.7 <sup>e</sup>
36.76	60.2	63.0	75.0	9.0	1.45	88.2		0.25	0.33	0.58

<sup>a</sup>The ammonium chloride was added 15 to 20 minutes after completion of addition of sodium to the liquid ammonia solution of allyl chloride.

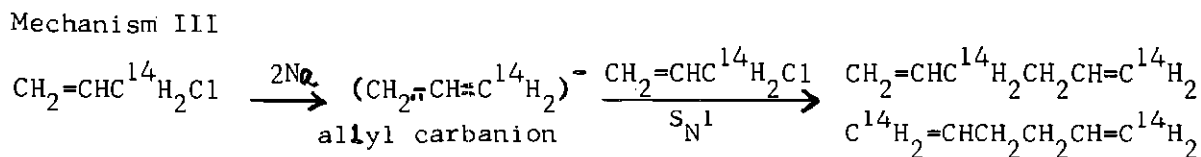
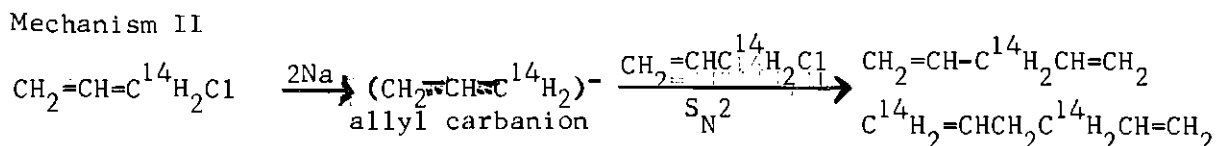
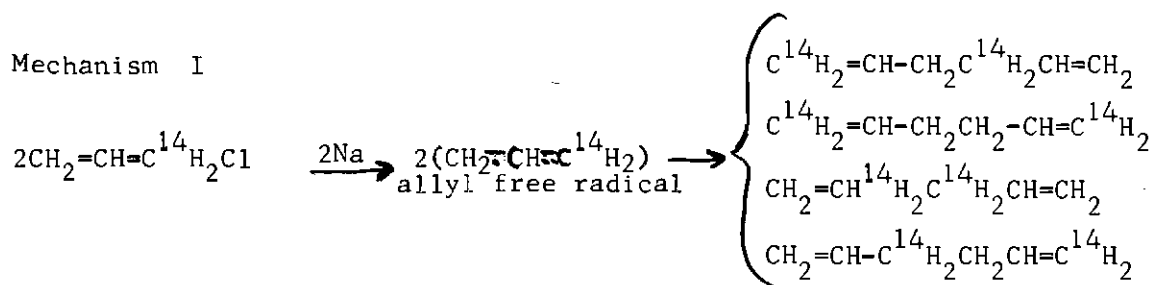
<sup>b</sup>Yield of bialllyl and isomers was based on the weight of material condensed in the trap cooled by liquid nitrogen and is calculated on the basis that 2 moles of allyl chloride give one mole of bialllyl

<sup>c</sup>The symbols I, II, B, III, IV, V, and VI refer to the components obtained at retention time of 7.8, 9.1, 10.5, 20.5, 29, 33.6, and 36.5 minutes respectively on Perkin-Elmer column "E", v.p.c. machine I, at 33°, 15 psi, and 43 ml./min. flow rate with helium as sweep gas. Component "B" is bialllyl.

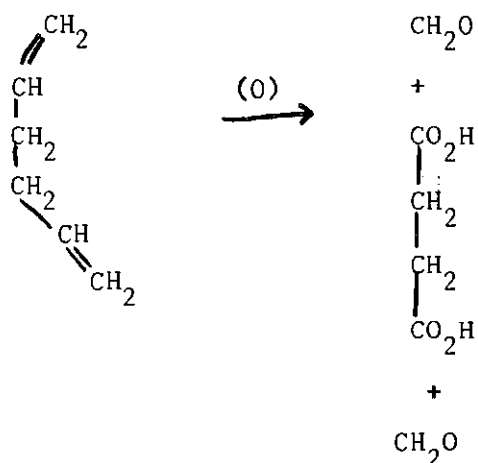
<sup>d</sup>Probably some bialllyl and isomers were lost because of lack of familiarity with the reaction system.

<sup>e</sup>This mixture was analyzed on column "E" on v.p.c. machine II at 33°, 15 psi, and 40 ml./min. flow rate of helium. Components I, II, B, IV, V, and VII had retention times of 10, 11.4, 13.5, 30.4, 48.6, and 61.5 minutes.

<sup>f</sup>These figures give the yields of bialllyl and isomers of the above reaction in terms of the peak heights as a comparison to the peak area method. The first two analyses in the table are also determined by the peak height, assuming that the height is linear with the amplification and that the height per millimole is the same for all compounds. It is seen that the components with longer retention times vary greatly from the yields as determined by peak area.



As shown here the three likely mechanisms give different distributions of carbon-14 in the bialllyl produced. The distribution of carbon-14 in the bialllyl can be ascertained by controlled oxidation to formaldehyde and succinic acid:



According to Mechanism I, the bialllyl results from dimerization of the



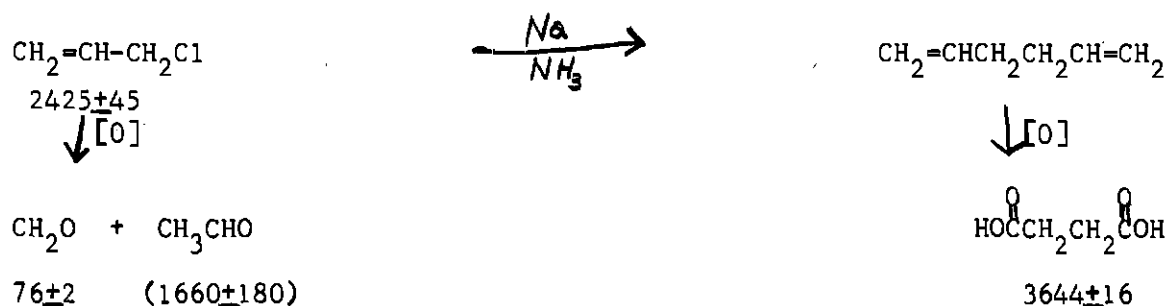
symmetrical allyl free radical. Oxidation of the biallyl should give formaldehyde with one-half and succinic acid with equal molar activity to that of the starting allyl chloride. For Mechanism II, which consists of an  $S_N2$  attack of symmetrical allyl carbanion upon allyl chloride, the resultant formaldehyde should have one fourth of the molar activity of the starting allyl chloride and the succinic acid three halves of the molar activity of the allyl chloride. For Mechanism III, which consists of  $S_N2'$  attack ("abnormal" nucleophilic displacement of chloride by attack at the methylene group most remote from chlorine) by symmetrical allyl carbanion, the formaldehyde should have three fourths of the molar activity of the allyl chloride and the succinic acid one half of this activity. It would be thought in advance that mechanism  $S_N2'$  would be less likely to occur than mechanism  $S_N2$  since mechanism  $S_N2'$  is generally observed to occur to an appreciable extent only when bimolecular substitution at the  $\alpha$ -position of the allyl derivative (but not at its  $\gamma$ -position) is retarded by steric hindrance.<sup>46</sup> Finally it should be noted here that these estimates of the amount of radioactivity in the products from the different mechanisms ignore any isotope effects.

In a preliminary experiment (Run I) reaction of allyl-1- $C^{14}$  chloride with sodium in liquid ammonia gave biallyl which after purification by vapor phase chromatography and oxidation gave succinic acid with the molar activity indicated in Chart I (where activities are written below the formulas in units of microcuries per millimole  $\times 10^4$ ).

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46. J. Hine, "Physical Organic Chemistry," 2nd edition, McGraw-Hill Book Company, Inc., New York, N.Y., 1962, pp. 152-154

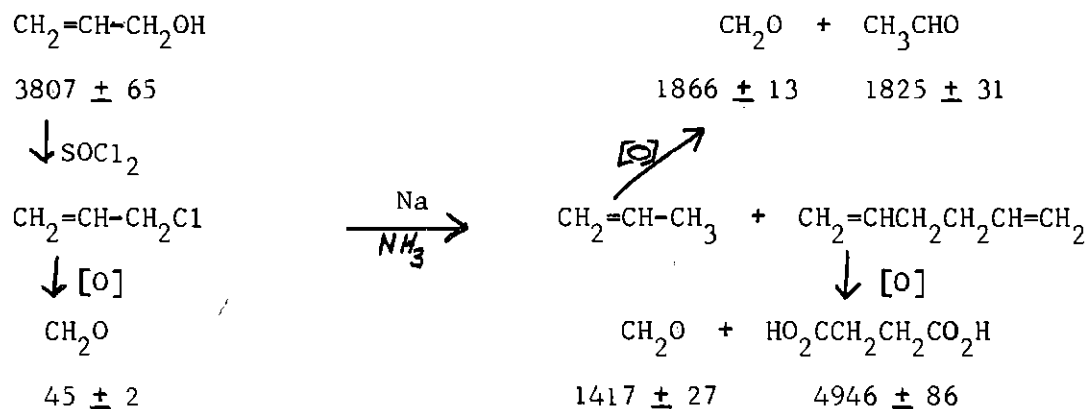
Chart I



These results give a ratio of molar activity of succinic acid to allyl chloride of 1.47-1.54 which is about the value expected for mechanism II ( $\text{S}_{\text{N}}2$ ). However because of an inadequate number of combustions of some of the samples, the indirect method of assay of the activity of the starting allyl chloride, the poor agreement in the assay of the derivative of acetaldehyde from allyl chloride, and the variability of the cell constant used in calculation of activities, the ratio is possibly less reliable than indicated. Consequently the reaction of radioactive allyl chloride with sodium in liquid ammonia was repeated.

The second run gave a distribution of carbon-14 in the products and reactants as summarized in Chart II (where again the activities are given in units of microcuries per millimole  $\times 10^4$ ). The sum of the molar activities of the formaldehyde and the acetaldehyde from the propylene is  $3691 \pm 44$ . The sum of the molar activity of the formaldehyde and half the molar activity of the succinic acid from the diallyl is  $3890 \pm 70$ . The former sum is 3.0 per cent lower and the latter sum 2.2 per cent higher than the molar activity of the starting allyl alcohol. While conceivably some isotopic fractionation to give enrichment of activity in the diallyl and

Chart II

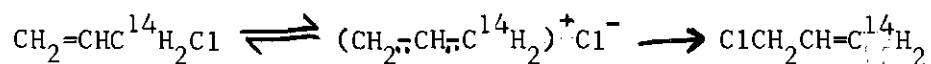


depletion of activity in the propylene might have occurred, the results should probably be taken as agreeing within likely experimental error with the activity of the starting allyl alcohol.

In the present run the ratio of the molar activity of the biallyl to that of the starting allyl chloride (equating the activity of the allyl chloride to that of the starting allyl alcohol) is 1.30. This ratio is intermediate between that expected for the  $\text{S}_{\text{N}}2$  mechanism (mechanism II) and the free radical or  $\text{S}_{\text{N}}2'$  mechanisms (mechanisms I or III respectively). A more detailed calculation (see Appendix C) shows that the present results can be interpreted on the basis that some  $22 \pm 3$  per cent of the reaction leading to biallyl proceeded by mechanism  $\text{S}_{\text{N}}2'$  with the remainder going by mechanism  $\text{S}_{\text{N}}2$  or alternatively  $43 \pm 5$  per cent proceeded by the way of the free radical mechanism with the remainder by mechanism  $\text{S}_{\text{N}}2$ . The most definite conclusion from both runs with allyl- $1\text{-C}^{14}$  chloride is that at least half

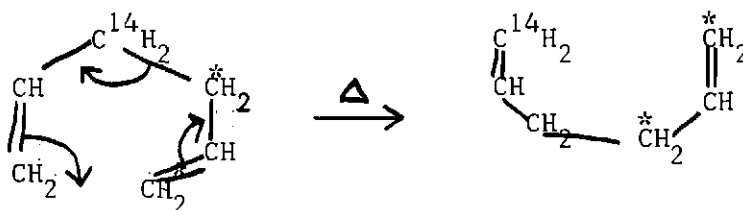
of the bialllyl produced is formed by mechanism  $S_N2$ . Other explanations can be given for the increased radioactivity of the formaldehyde and decreased radioactivity of the succinic acid formed from bialllyl than for reaction by mechanism I and III.

One alternative explanation is that allyl chloride undergoes ionization in liquid ammonia solution to give an intimate ion pair which undergoes internal return in part with rearrangement:



While analogous reactions are known<sup>47</sup> in the acetolysis of  $\alpha,\alpha$ -dimethylallyl chloride, such an explanation appears unlikely in the present case because of the low temperature ( $-70^\circ$ ) and short contact time 20 to 25 minutes all allyl chloride with liquid ammonia before reaction with sodium is complete. Moreover if ionization in fact occurred, much ammonolysis to allyl amine would be expected and therefore the yields of hydrocarbon products would likely not be as great as generally found.

A second alternative explanation is that the bialllyl formed underwent in part a Cope rearrangement prior to ozonolysis.



47. W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

Such Cope rearrangements, as for 3-phenyl-1,5-hexadiene, generally require temperatures of about 180°, while 3-methyl-1,5-hexadiene (which is somewhat more similar to bialllyl) required a temperature of about 300° to effect rearrangement.<sup>48</sup> In the present work the sample of bialllyl was kept at room temperature or below at all times save during the purification by vapor phase chromatography. During the latter process the column was operated at 33° while the flash evaporator was at least as high as 43°. In fact a sample of bialllyl when put through the preparative v.p.c. apparatus gave the analysis given in Table 9 before and after such treatment as determined by the analytical v.p.c. column. It seems significant that while the preparative v.p.c. column appears to have given surprisingly little purification of the bialllyl, yet it completely removed bialllyl isomer IV without removing bialllyl isomers of longer retention time. The most likely interpretation appears to be that while the preparative v.p.c. apparatus removed all of the bialllyl isomers of high retention time, the flash evaporator in the analytical v.p.c. apparatus somehow restored most but not all of these isomers. It seems likely that if the v.p.c. apparatus can bring about isomerization of bialllyl to chemically different isomers that it can also bring about the generally more facile Cope rearrangement.

The occurrence of some bialllyl isomers in the bialllyl which was ozonized should not invalidate the present tracer experiment unless,

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48. H. Levy and A. C. Cope, *J. Am. Chem. Soc.*, **66** 1648 (1944).

TABLE IX

Analysis of Biallyl<sup>a</sup>

Component:	I	II	B	IV	V	VII
Retention time (min.)	10	11.4	13.5	30.4	48.6	61.5

## Per cent of components in mixture

Analysis of unpurified biallyl	9.4	1.4	88.0	0.4	0.7	1.7
Analysis of purified biallyl <sup>c</sup>	5.3	0.5	91.9	-- <sup>b</sup>	0.5	1.8

<sup>a</sup>The analysis is based on the area contained under the curves and weighted according to the amplification of the recorder assuming that the area is in direct proportion to the amplification. Moreover it is assumed that all of the components give the same peak area per millimole.

<sup>b</sup>This isomer was not detected; therefore less than 0.1 per cent was present.

<sup>c</sup>This sample of biallyl was supposedly purified by injecting a sample of biallyl into preparative column "E" and collecting the major biallyl fraction as it came out of the machine in a condenser inserted into a dry ice-acetone cold trap.

like for the Cope rearrangement, isomerization occurs with migration to carbon skeleton. Rearrangements of positions of double bonds, cyclization to cyclopentene derivatives and the like which occur without cleavage of carbon-carbon bonds should not invalidate the present tracer experiments since the products of such isomerization either do not give formaldehyde and succinic acid on oxidation or else they give formaldehyde with unaltered activity relative to the starting biallyl (neglecting isotope effects).

In conclusion it appears likely that most or all of the diallyl formed by reaction of allyl chloride with sodium in liquid ammonia is formed by  $S_N2$  attack of allyl carbanion upon allyl chloride.

## APPENDICES



## APPENDIX A

## DETERMINATION OF SPECIFIC ACTIVITIES

To measure the ionization chamber current two methods were used.

Steady Deflection Method.--The ionization chamber was set on the head of the vibrating-reed electrometer. The amplifier was set at a suitable amplification. The turret switch was turned from ground to position 4 to connect the system with the high-resistance-leak resistor ( $10^{12}$  ohms). The electrometer system was allowed to come to its equilibrium voltage. This voltage was recorded, and the background voltage was subtracted from it. This method was not relied upon too heavily since the reading varied because of noise and background such that a good average value was hard to obtain.

Rate of Drift Method.--The ionization chamber was set on the head of the vibrating-reed electrometer. The amplifier was set at suitable amplifications. The turret switch was turned from "ground" to "open" position. The interval of time was recorded as the pointer in the Brown Recorder moved from 8 to 88. The process was repeated 7 to 10 times for the same sample in the ionization chamber, and an average value (time in seconds) was calculated. As the time for charging the condenser is inversely proportional to the current, a conversion factor was used to convert time into current. To obtain the value of the conversion factor, readings were taken by both methods on the same

sample in the ionization chamber.

Calculation of Molar Activity.--On the sample of carbon dioxide collected in the ionization chamber after combustion of a standard sample of benzoic-C<sup>14</sup> acid, the following observations were made:

Voltage (by steady deflection method):

0.0705 volts

Average time on 1 volt scale (by rate of drift):

117.3 seconds

Conversion factor: (voltage = (conversion factor)/time

$0.0705 \times 117.3 = 8.28$  volt-seconds

Specific activities of radioactive compounds were calculated in microcuries per millimole by the formula:

The molar activity in microcuries per millimole is given by the quotient:

$$\frac{(\text{potential difference in volts}) (\text{molecular weight of sample})}{(\text{cell constant})(\text{weight of sample in milligrams})}$$

The cell constant is obtained by burning a sample of standard benzoic-C<sup>14</sup> acid obtained from Chem Trace Corporation, Cambridge, Mass. The readings were taken by both methods to obtain the conversion factor. The same conversion factor was then used for all combustions since, in fact, the conversion factor will cancel out in calculation of molar activity. The cell constant, on the other hand, was determined for each series of combustions.

A typical determination of specific activity, showing numerical data, follows. The data were taken from the combustion of the formal-

dehyde derivative from isomerization of allyl-1-C<sup>14</sup>-trimethylammonium chloride. The analysis comes from Table 6, the second analysis.

Weight of formaldimethone:

7.47 mg.

Average time on 1 volt scale:

294.93 seconds

Calculated voltage:

0.02807 volts

Calculated voltage after subtracting background voltage:

$0.02807 - 0.00068 = 0.01739$  volts.

Molecular weight of the formaldimethone

292

Specific activity of the formaldimethone

$$\frac{0.02739 \times 292}{5.36 \times 7.47} = 0.1996 \text{ microcuries per millimole.}$$

## APPENDIX B

## CALCULATION OF APPARENT PER CENT ISOMERIZATION OF ALLYLTRIMETHYLAMMONIUM CHLORIDE

Total activity of allyltrimethylammonium chloride = 0.3475 microcuries per millimole.

Calculated activity = 0.1738 microcuries per millimole for formaldehyde obtained from propylene formed from allyltrimethylammonium ion (ignoring isotope effect in protonation.)

Isotope effect = 1.056 as previously determined by Chandra<sup>45</sup> for average observed ratio of activity of formaldehyde to activity of acetaldehyde.

$$1.056 = \frac{0.1738 + Y}{0.1738 - Y}$$

$$Y = 0.0047$$

Y = increment in activity due to isotope effect in protonation of allyl carbanion

$$\text{Fraction of isomerization before reaction} = \frac{0.0042}{0.3475} = 0.012$$

where 0.0042 is the activity of the formaldehyde obtained by ozonization of the allyltrimethylammonium chloride.

If we let X = mole fraction of isomerized quaternary salt, then making a calculation based on the activity of the formaldehyde acetaldehyde (0.1976/0.1476) obtained from propylene from the quaternary salt:

$$\frac{0.1976}{0.1476} = 1.34 = \frac{(0.3475)(0.988)(X) + (1-X)(0.1785)}{(1-X)(0.1691) + (0.012)(0.3475)(X)}$$

$$X = 0.123 \text{ or } 12.3 \text{ per cent isomerized}$$

The answer is corrected for isotope effect in protonation of allyl carbanion and for rearrangement during preparation of quaternary salt.

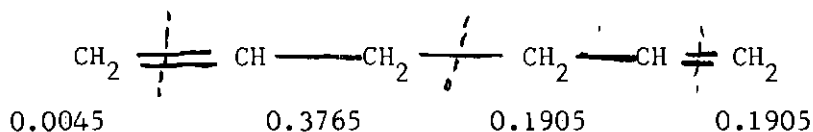
This calculation assumes that isomerized allyl-1-C<sup>14</sup>-trimethylammonium ion, i.e., propenyl-1-C<sup>14</sup>-trimethylammonium ion, gives exclusively propylene-1-C<sup>14</sup>, that enough alkali metal is present to cleave all allyl and propenyl compounds; that alkyl and propenyl compounds give the same yield of propylene; and that isotope effects (other than that corrected for) are unimportant.

## APPENDIX C

## CALCULATION OF PER CENT REACTION BY VARIOUS MECHANISMS

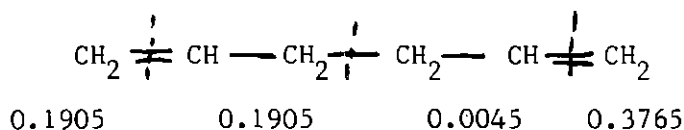
The per cent of  $S_N2$  reaction that must have taken place along with  $S_N2'$  or free radical reaction can be calculated in the following manner. By using the measured molar activity of the allyl-1- $C^{14}$  alcohol and the calculated values of the molar activity of formaldehyde and succinic acid as calculated for the proposed mechanisms, the per cent of possible reaction by each mechanism can be calculated from the measured activity of the formaldehyde and succinic acid from the biallyl produced.

The  $S_N2$  mechanism, based on allyl-1- $C^{14}$  alcohol, should give biallyl with the following distribution of activity in microcuries per millimole in Run II (with due consideration being given to the apparent amount of allyl-3- $C^{14}$  alcohol present).



For the formaldehyde, the activity would be  $(0.1905 + 0.0045)/2 = 0.0975$  microcuries per millimole. For the succinic acid, the activity would be  $0.3765 + 0.1905 = 0.5670$  microcuries per millimole.

From similar data for the  $S_N2'$  mechanism the following distribution of molar activity can be calculated for biallyl:



For formaldehyde the molar activity would be  $(0.1905 + 0.3765)/2 = 0.2835$  microcuries per millimole while the succinic acid would have  $(0.1905 + 0.0045)/2 = 0.1950$  microcuries per millimole.

Using the experimental values obtained by analysis for formaldehyde and succinic acid we can set up equations for the fraction by different mechanisms.

Let  $X$  = fraction of reaction via  $S_N2'$  mechanism.

Let  $(1-X)$  = fraction of reaction via  $S_N2$  mechanism.

$$\begin{aligned}
 \text{Based on formaldehyde } (X)(0.2835) + (1-X)(0.0975) &= 0.1417 \\
 0.2835X + 0.0975 - 0.0975X &= 0.1417
 \end{aligned}$$

$$X = 0.238 \text{ or } 23.8 \text{ per cent } S_N2'$$

$$\begin{aligned}
 \text{Based on succinic acid } X(0.1950) + (1-X)(0.5670) &= 0.4946 \\
 0.1950X + 0.5670 - 0.5670X &= 0.4946
 \end{aligned}$$

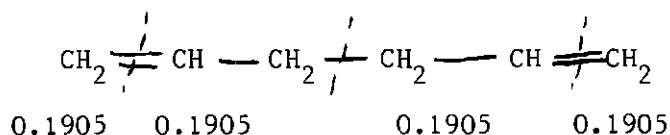
$$X = 0.1945 \text{ or } 19.45 \text{ per cent } S_N2'$$

By using the upper and lower extreme activities for formaldehyde and succinic acid, by similar calculations the following limits may be set for reaction by the two mechanisms:

$$\text{Based on formaldehyde} = 23.8 \pm 1.1\% S_N2'$$

$$\text{Based on succinic acid} = 19.45 \pm 2.4\% S_N2'$$

The distribution of molar activities in biallyl formed by the free radical mechanism is similarly estimated to be as follows in Run II.



For formaldehyde the activity would be  $0.381/2 = 0.1905$  microcuries per millimole. For succinic acid the molar activity would be  $(0.1905 + 0.1905) = 0.381$  microcuries per millimole.

Let  $X$  = fraction of reaction by free radical mechanism.

Let  $1-X$  = fraction of reaction by  $S_N2$  mechanism.

Based on formaldehyde  $(X)(0.1905) + (1-X)(0.0975) = 0.1413$

$X = 0.470$  or 47.0 % by free radical mechanism

Based on succinic acid  $X(0.381) + (1-X)(0.5670) = 0.4946$

$X = 0.389$  or 38.9% by free radical mechanism

From the extreme values of the measured activities of formaldehyde and succinic acid the following limits may be set for reaction by the two mechanisms:

Based on formaldehyde =  $47.3 \pm 1.8\%$  by free radical mechanism

Based on succinic acid =  $38.9 \pm 3.1\%$  by free radical mechanism.

The above calculations are based on the assumption that the measured molar activity and distribution of activity are correct for the starting allyl alcohol and allyl chloride. Moreover these calculations ignore any isotope effects during reaction of these compounds and assume that completely symmetrical (*i.e.*, kinetically free) allyl carbanions and radicals are formed as intermediates.



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